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ONTARIO
INDUSTRIAL WASTE
CONFERENCE

Proceedings

JUNE 1964

SPONSORED BY

THE WATER AND POLLUTION ADVISORY COMMITTEE

TO THE

ONTARIO WATER RESOURCES COMMISSION

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PREFACE



D. S. Caverly,
General Manager,
Ontario Water Resources Commission,
Toronto.

Conference Chairman

1964 saw the 11th Ontario Industrial Waste Conference in a new location at Bigwin Inn, Lake of Bays, Ontario, and this helped to make our meeting distinctly successful.

It was a pleasure to meet with old friends again and to welcome so many new ones to our annual meeting on the vital subject of industrial wastes. The Water and Pollution Advisory Committee is grateful to those who prepared and presented papers and to those who participated in the discussions. The exchange of information and ideas together with free discussion is the key to our progress in solving many disturbing problems created by Industry's wastes.

This Proceedings records all the papers presented at the meeting together with the Banquet Address by Professor Marcus Long, of the University of Toronto, to whom we are indebted for an inspiring evening.

Encouraging results have been achieved to date in the abatement of industrial pollution and the Committee is anxious to promote further co-operation among all concerned to achieve the highest degree of purity in the rivers and streams of Ontario.

Further information may be obtained from the Water & Pollution Advisory Committee, Ontario Water Resources Commission, 801 Bay Street, Toronto 5, Ontario.

THE WATER AND POLLUTION ADVISORY COMMITTEE

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SESSION ONE



A. V. Delaporte

Session Chairman

"ACTIVATED SLUDGE APPLICATION
TO CHEMICAL INDUSTRY WASTES"

by

B. W. DICKERSON

Waste water treatment is expensive. Its cost, facilities and operation is today an integral part of plant and product cost and is so recognized by industry. In today's keen competition it is paramount that the program selected will be the most economical, consistent with effective waste reduction.

Industrial wastes seldom result from one operation. They are usually components from many processes, each with its own particular characteristic. The organic material may thus become one of several compounds, all of which must be included in the overall treatment picture and each of which may have a pertinent bearing on the solution.

It is, therefore, necessary that serious consideration be given to all phases which may be present, since these can easily alter ultimate treatment as well as inject complicated pretreatment requirements into the biological purification program.

Today, industry has proven that the activated sludge type plant will treat most industrial wastes economically with high efficiency and a minimum of supervision.

Toxic materials are handled as effectively by activated sludge as with trickling filters and in some cases more so. When compounds are extremely slow in breaking down, activated sludge proves the only effective means of treatment.

It is seldom that soluble organic wastes are in such condition that pretreatment is not required. These can be settleable solids, free oil, oily emulsion, and acidic or alkaline pH concentration. Widely varying flows may also require control. Necessary facilities must be provided for all of these that their influence will not interfere with proper biological oxidation.

Biological oxidation is usually most active in the pH range of 7.0 to 8.0. This does not mean that for a highly acid or alkaline waste initial neutralization must be brought into this exact range. Depending upon the character of the waste and its oxidation, interaction and buffering may well raise or lower the resultant pH of the system into this range. Thus, pH correction may only need to be brought up to 6-6.5 or down to 9-9.5.

While lime, either burned or hydrated, is the cheapest alkali for neutralization, reaction products may well dictate the use of soda ash or caustic. This must be determined from individual studies.

Unless a knowledge of the constituents present and the BOD work has indicated there is no problem of toxicity or bacteriostatic lag, these two phases should be investigated. Here the Warburg respirometer provides an effective tool in developing the answers.

Oxygen uptake curves should be run on a series of concentrations from 1% to 50% using sanitary sewage as the substrate. The curves developed will show not only limiting toxicity values but any bacteriostatic lag. Since this work is carried out with sewage, the values developed will be minimal and higher values will usually be obtained from acclimatized organisms. Using the maximum per cent developed for toxic threshold, acclimatization of the organisms should be carried out by aeration of the waste substrate and sewage seed for a period of two to three weeks. Warburg studies should again be made. A new set of curves will be developed showing much higher limits, sometimes no toxicity at all at full strength. In this work, the pH should be adjusted to about 7.5

For optimum bacterial metabolism, nitrogen and phosphorus are required. Most industrial wastes are low or lacking in these. It is necessary that they be added in the required amounts. Normally, the BOD:N ratio is about 20:1 and BOD:P ratio about 40:1. The Warburg will allow determination of these values. Runs are made holding P constant and using 0-50-100% of the N20:1 ratio. Then, the work is repeated with N constant and varying 0-50-100% of the P40:1 ratio.

In activated sludge studies it is necessary to know the time required for aeration. For this, batch aeration tests are carried out. Here again, an acclimatized sludge is necessary. The aeration unit can be a 2 litre graduate provided with a frittered glass sparger in the bottom. The maximum strength waste is used with the acclimatized sludge added to provide a concentration of 2,000 ppm suspended solids. The unit is operated for 24 hours and samples taken at 1, 3, 6, 10, 15, 20 and 24 hours and analyzed for BOD as well as COD. A curve is plotted from the data developed. This will show the degree of purification which can be obtained for various aeration periods.

The next step is to determine sludge solids concentration for maximum purification. The Warburg unit is again used. Using the optimum time of aeration, oxygen uptake is determined with varying solids concentration. The suspended solids concentrations should range from 800 to 4,000 mg/l. The BOD values are determined and data plotted. With feed concentration and efficiency required, optimum solids concentration can be selected.

Most industrial wastes are normally at atmospheric temperature or a little higher in summer. There are plants where the waste water temperatures may be above 40°C. While there will be atmospheric cooling during the winter months, there will be very little reduction in the summer. It is, therefore, essential to know whether such temperatures will be detrimental to operation of the treatment plant. Warburg studies should be run covering the range of 25°C through the maximum to be experienced. This will show what the limit must be.

For those waste streams which are highly acid or alkaline, pH correction is necessary. Titration studies should be carried out and the curves plotted. Where waste acid or alkali may be available for neutralization, similar curves should be developed. Where large volumes are to be neutralized prior to biological treatment, rate reaction curves are necessary.

After the laboratory phase has been finished, semi-pilot work will carry out, on a continuous flow basis, the concepts developed from the laboratory. Bench scale units are used here. These can be made of plastic or metal, either circular or rectangular in shape. After this work has been completed, a full scale pilot study can be carried through to develop, in more detail, design criteria for full scale plant operation. Let us now examine some chemical wastes from the laboratory studies through semi-pilot work and full scale operation.

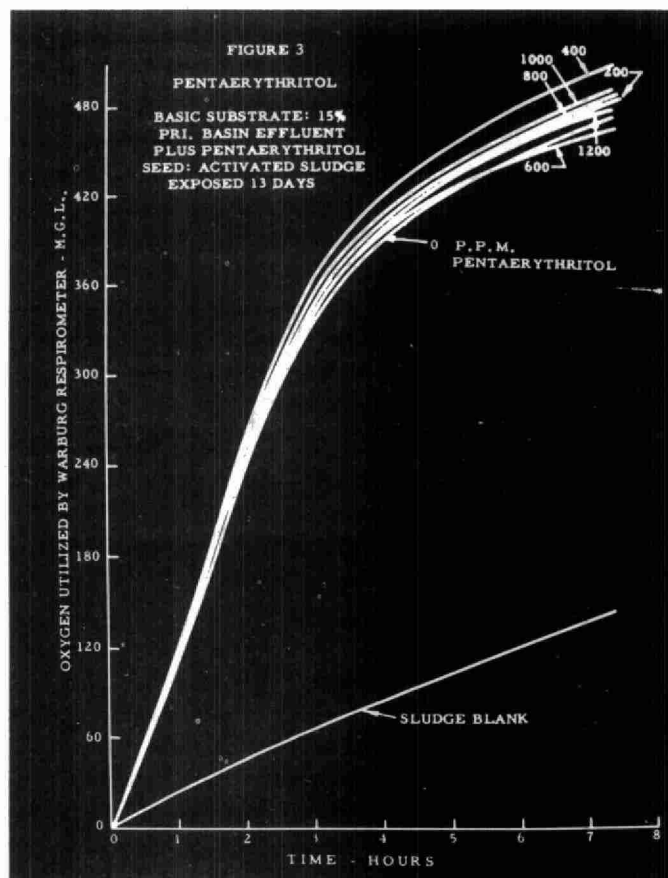
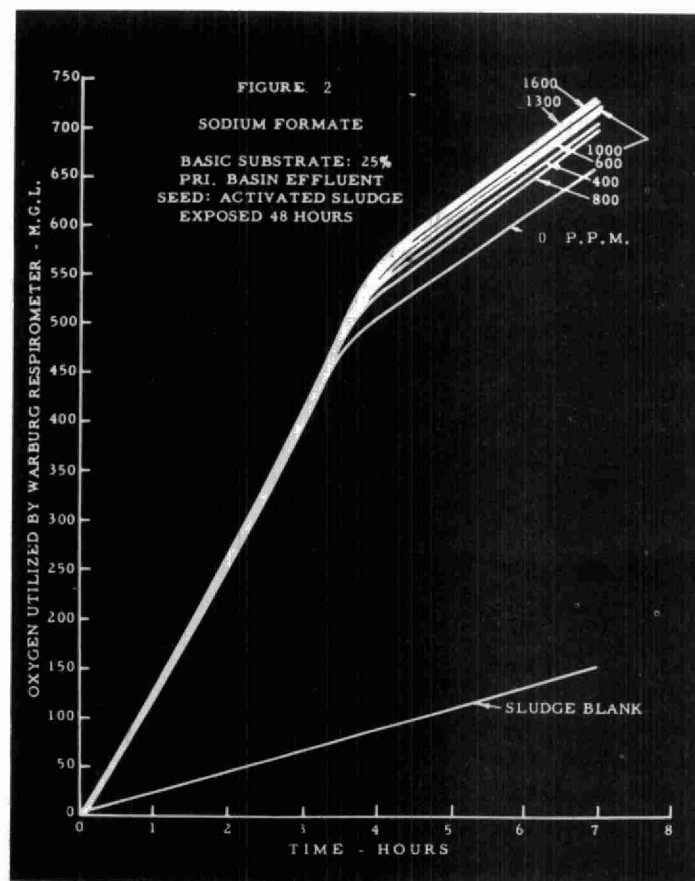
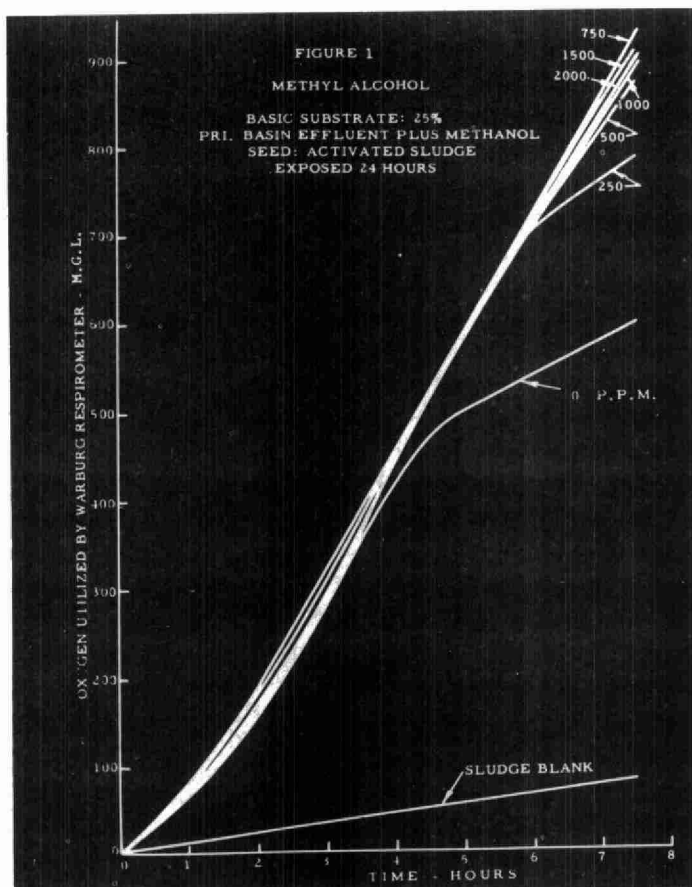
The Mansfield, Massachusetts plant produced pentaerythritol, the waste water of which contained formaldehyde, methanol, sodium formate and pentaerythritol. Originally of small production capacity, the waste effluent was effectively treated on a high rate trickling filter. The total BOD load was about 600 lbs. per day.

When plant operations were expanded, the new BOD loads were calculated at about 3,000 lbs. per day and another trickling filter was constructed, based on existing operating data. When the system was placed in operation, the BOD load was found to be about 5,000 lbs. per day. Filter efficiency was poor with purification less than 50%. Since there had been no change in manufacturing operations, a complete investigation of the raw wastes and trickling filter effluents was made to determine the origin of the trouble.

A very high percentage of methanol was found in the raw waste water which had not been contemplated. Re-examination of the raw materials showed that, where previously less than 1/2% methanol was present in one of them, the value was now over 3%. Thus, in addition to a formaldehyde concentration of some 2500-3000 mg/l, there was a methanol concentration of some 3000 to 4000 mg/l. This was felt to be the cause of the poor operation. The overall picture was further aggravated by extremely low dry weather flows in the receiving stream.

Because of the change in conditions, it was felt that new toxic thresholds should be developed for all the waste constituents. The Warburg respirometer was used for this work. An activated sludge seed was developed for each of the waste constituents and this was the seed used in the Warburg studies.

Oxygen uptake studies were made on methanol, sodium formate and pentaerythritol. These curves, Figures 1, 2, and 3, show no evidences of toxicity.



Because of the need for heat conservation during the winter months, it was felt that an activated sludge unit would keep these losses to a minimum. This, together with the ability to design into it any aeration period necessary, dictated this selection for the required third stage of treatment. A semi-pilot unit employing a 50 gallon aeration tank was constructed and operated over a period of three months to develop design criteria for the full scale plant addition.

This unit was operated initially on formaldehyde only and therefore on the existing treatment plant secondary trickling filter effluent, since this would be the feed for the full scale activated sludge unit. Primary basin effluent was used as the initial mixed liquor in the semi-pilot unit and acclimatized to the particular waste stream.

The unit was operated with a feed of 3,000 mg/l formaldehyde and an aeration period of 24 hours. This study showed that, when the pH of the mixed liquor was held at 7.2, 99% of the formaldehyde was removed and 95% of the BOD. As the pH was lowered to 6.0, formaldehyde removal remained at 99% but BOD removal was only 80%. As the pH was lowered to 4.6, formaldehyde removal dropped and BOD removal dropped to zero. When the pH was re-adjusted to 7.2 both formaldehyde and BOD removals returned to the original high levels.

This work showed pH adjustment was necessary and reflected the conversion of formaldehyde to formic acid by the bacteria as the pH was lowered. It provided an answer to the low pH conditions that had developed in the primary trickling filter and the high BOD in the primary effluent. Figure 4 shows this pH change.

Warburg studies were made on formaldehyde using NaHCO_3 as a buffer. Figure 5 shows no problems of toxicity up to 1,500 mg/l.

The pilot activated sludge unit was operated on secondary filter effluent at various rates of feed, aeration periods and mixed liquor solids. From this work, it was found that 24 hours was the optimum period of aeration and with solids of 2500-4000 mg/l in the mixed liquor, 80% reduction in BOD could be obtained. During this work, it was felt that variations in mixed liquor temperature should be investigated. Figure 6 shows the effect of this on BOD removal.

Time was most essential and to expedite construction a wooden tank with a concrete bottom was used. A rectangular section in the central portion provided the settling basin area. Low walls of concrete for this, with wood staves above, formed the basin and allowed the installation of a mechanical sludge collection system. Retention time was 3 hours. The aeration section utilized the space between the tank walls and the settling portion. This was provided with an impingement nozzle aeration system. The liquid flow was in a circular path completely around the tank and then into the settling section. Aeration time provided 24 hours retention. The tank was 40 feet in diameter and provided 16 feet of water depth.

With this equipment added, the treatment system then comprised two stages of high rate trickling filters, followed by one stage of activated sludge, providing 24 hours aeration. The average flow was 75 gpm.

In operation, the free formaldehyde was almost completely broken down in the primary unit. Methanol was broken down in the primary and about 40% removed there. In the secondary filter, 30% of the remainder was oxidized and in the activated sludge plant, about 93% of that remaining was oxidized. About 90% of the sodium formate was broken down in the secondary unit, and about 95% of that remaining was removed in the activated sludge unit. About 90% of the pentaerythritol was ultimately broken down in the activated sludge unit.

The following is a typical analysis of the raw waste feed:

BOD	9,400 mgl
COD	15,000 mgl
Sodium Formate	500 mgl
Methanol	2,880 mgl
Formaldehyde	3,500 mgl
Volatile Acids as CH_2O_2	500 ppm
Total Solids	876

Typical BOD values through the system were as follows:

Raw Feed	9,400 mgl
Pri. Effluent	2,100 mgl
Sec. Effluent	960 mgl
Act. Sludge Eff.	115 mgl

This picture of three stage treatment is rather unusual for a waste treatment system. It shows that activated sludge is a versatile tool that can be applied to an existing system for providing additional purification.

The Higgins Works, located at Gibbstown, N.J., produce synthetic phenol, acetone, paracresol and related products. The waste waters contain phenol, paracresol and oxidation products, a high pH and some free oil. Treatment was required and it became necessary to design and construct a purification plant.

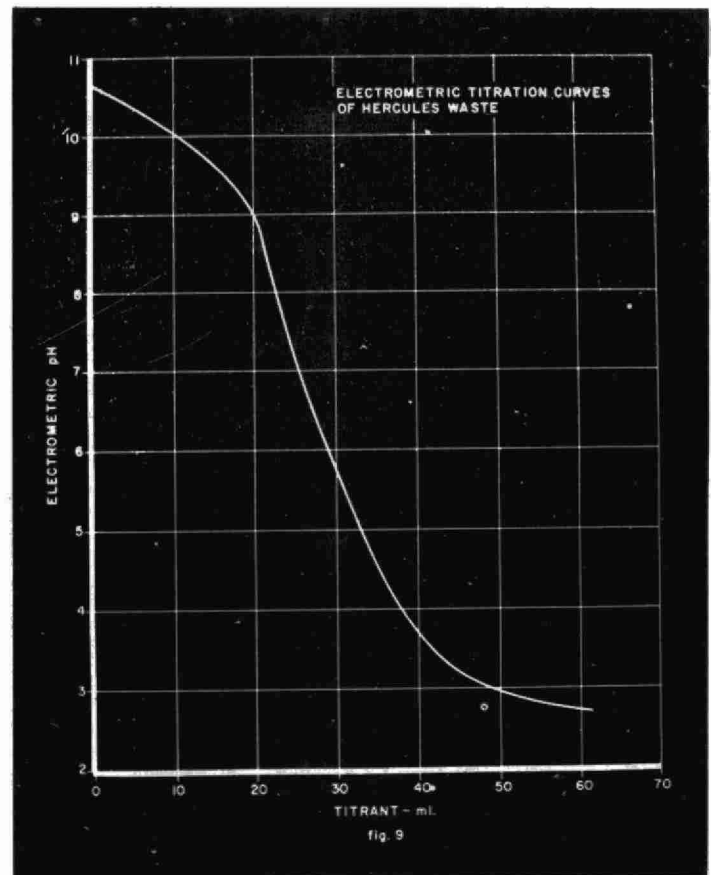
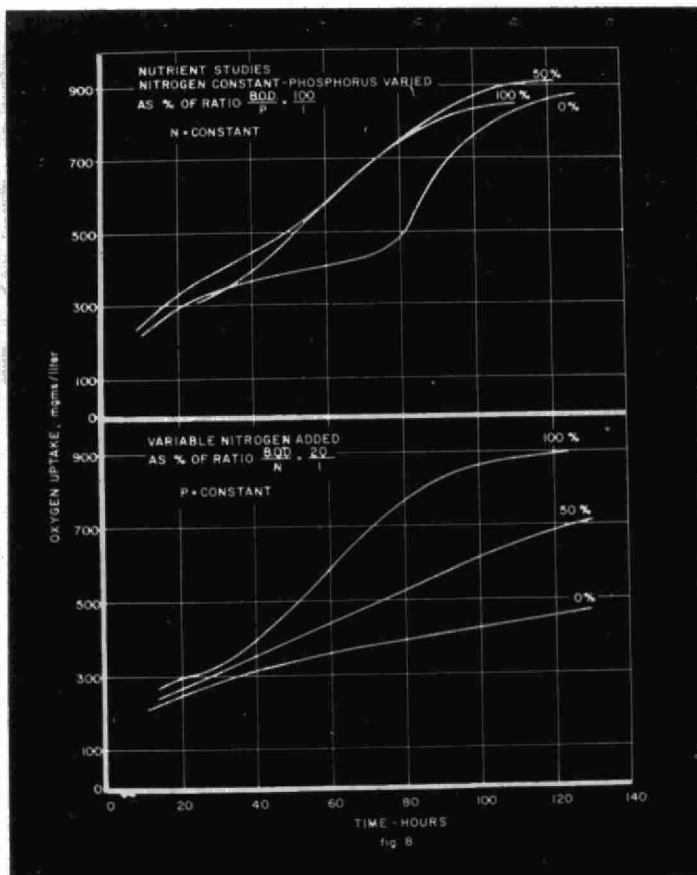
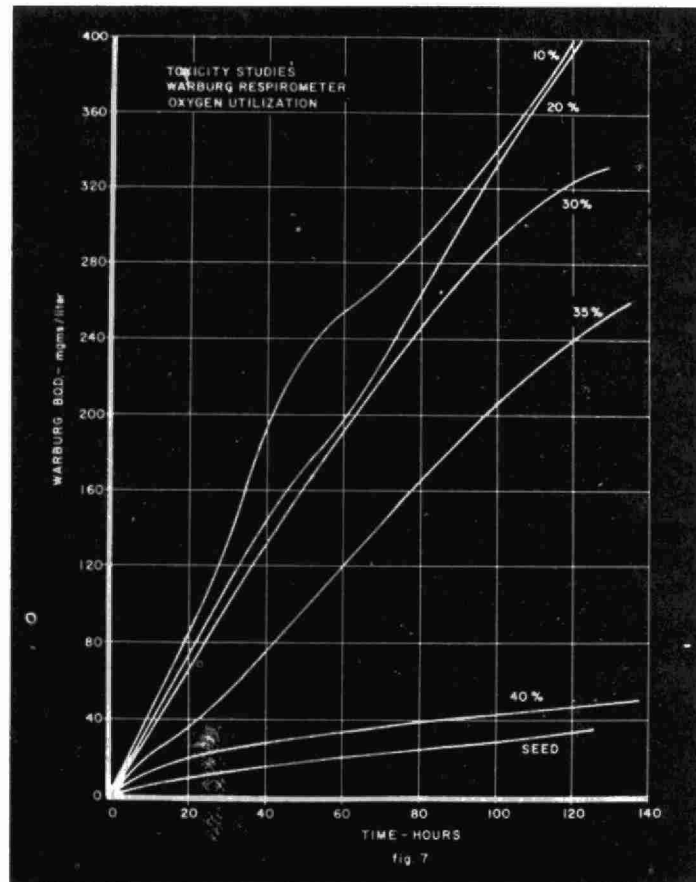
There were wide variations in concentration of the raw waste. Studies indicated an equalization basin would smooth out these variations and provide a satisfactory stream. A typical analysis is as follows:

BOD	2,300 mgl
COD	3,470 mgl
Phenol	540 mgl
pH	10.5
Nitrogen	nil mgl
Phosphorous	nil mgl
Total Solids	4,250 mgl
Volatile Solids	1,300 mgl
Fixed Solids	2,950 mgl

The first phase of laboratory study was to determine toxicity thresholds. Runs were made on a Warburg respirometer with various concentrations of raw waste and a series of curves developed. Figure 7 shows the results. Toxicity is not a factor until concentrations over 35% are experienced.

The waste was deficient in both N and P. Warburg studies were made to determine the optimum values. The first held P constant and the N was varied from 0 to 100% based on a 20:1 BOD:N. The second held N constant at 20:1 and the phosphorus was varied from 0 to 100% based on a 100:1 - BOD:P. Figure 8 shows the results of these studies. A 20:1 ratio for N and 100:1 ratio for P were necessary.

The high pH of the waste water required neutralization with acid to bring it into range of the treatment system. Titration studies were carried out to determine the acid requirement. Figure 9 shows the curve developed using sulphuric acid.



Optimum sludge solids concentrations for various BOD feed concentrations were necessary for semi-pilot continuous flow studies. These were determined through a series of tests in which varying loads of solids from previously seeded batches were aerated in a shaking machine for 24 hours. The BOD was determined at the start and again after 16, 20 and 24 hours of aeration, followed by a brief settling period. Figure 10 shows the data developed and indicated that a solids concentration of about 4,000 mg/l would be optimum.

Continuous flow aeration studies were carried out in three 18 litre tanks provided with settling sections. A series of 18 runs were made in which aeration time was varied from 12 to 36 hours with BOD feed concentrations between 2300 and 2900 mg/l. The data developed from this work is shown in Table 1.

From the continuous flow studies, a 24 hour aeration period was felt to be optimum. With this constant, a performance curve was developed between BOD loading and removal based on lbs./1000 cu. ft. of aeration tank capacity. Figure 11 shows this relationship. From this data, a full scale plant was designed and constructed.

Because of the terrain, a central lift station was necessary to collect both the industrial and sanitary wastes and pump them to the treatment plant. Here pH correction was provided for the industrial waste using H_2SO_4 to reduce the pH to about 8.5. Diammonium phosphate feed was provided at this same location for nutrient addition of P and some N. The remaining N requirement was added as NH_4OH at the aeration tank.

Equalization was provided in a gunite lined earth basin holding about 1,000,000 gallons.

The aeration tank was circular in shape and constructed of redwood staves. It was 62 feet in diameter and had a water depth of 16 feet. The bottom was of concrete. A centre baffle provided two aeration sections with series flow. Impingement type aeration nozzles were installed along each side of the centre baffle. The tank provided 24 hours aeration of the raw waste plus return sludge.

The design flow was 150 gpm; the BOD load, 4,000 lbs. per 24 hours. Oxygen requirements were based on Warburg uptake studies and the air required was supplied by two 1,200 cfm centrifugal compressors providing 7 psi.

A sludge reaeration tank was provided in the system, together with a final settling basin and sludge return pumps. Figure 12 shows the flow sheet.

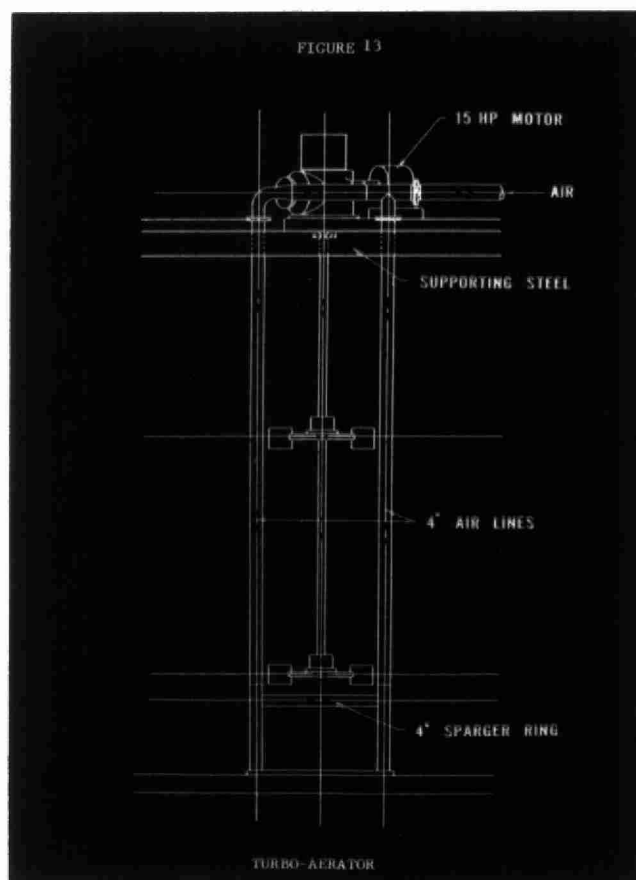
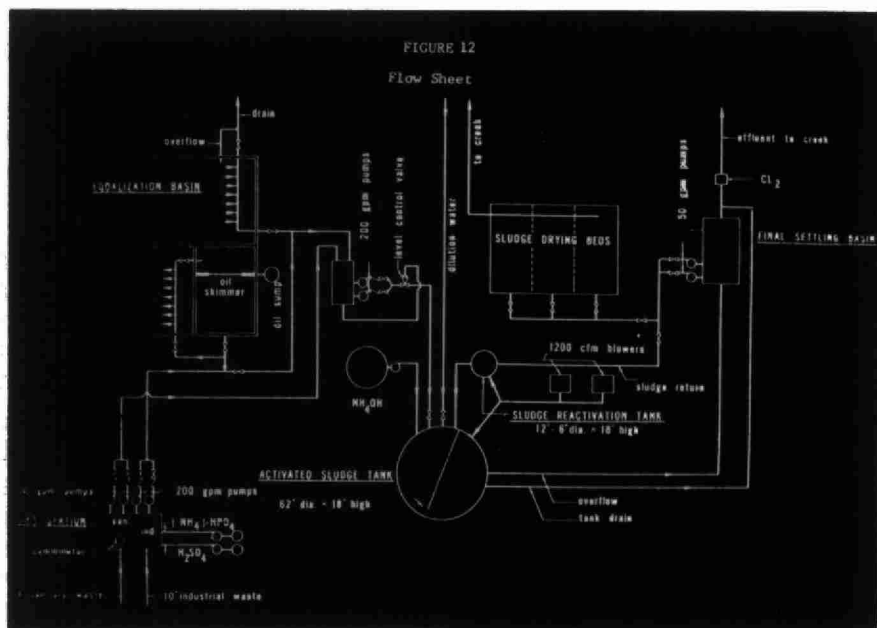
The aeration tank was seeded with 10,000 gallons of municipal digester sludge and the system gradually acclimatized to the waste. Phenol reduction was excellent, being about 99%, but BOD reduction averaged only 50%. Sludge solids could never be built up above 1,200 mg/l and this was felt to be the reason for low BOD reduction. Analyses showed the raw waste to be in line with earlier studies. It was believed that additional sludge solids should be provided and twenty-five thousand gallons of additional digester sludge were added to the aeration tank. The system then began to function properly. The BOD load was increased to 2,500 lbs. per day and 80% purification was obtained with excellent phenol reduction. However, attempts to raise the loading above this resulted in odours in the aeration tank, indicating lack of oxygen. The addition of the second blower did not improve operation. Detailed studies showed the oxygen transfer to be only 6%, whereas the calculations were based on 10%. This was insufficient to provide the oxygen required in the system. It was necessary to improve the oxygen transfer to handle the full load.

Turbo aerators were coming into use and these were investigated. It was felt that oxygen transfer efficiencies of at least 20% could be obtained. To try out this method of aeration and develop operating data, one 15 HP unit was purchased and installed in one quadrant of the tank, together with the air sparge ring and piping. Figure 13 shows the arrangement of the turbo aerator.

The effect of this new unit was apparent immediately. The full flow of waste was easily taken by the plant and 89% efficiency was obtained at a BOD load of 3,850 lbs. The oxygen transfer of this unit was calculated at 19%. Phenol efficiency remained good, the reduction being from 600-800 mg/l to 10-54 mg/l.

Shortly after this addition, process operations were expanded and the BOD loading increased to about 7,000 lbs. per day. (The volumetric increase for this load was small.)

Semi-pilot studies showed that the existing plant facilities would be satisfactory with some modifications. These were 3 more 15 HP turbo aerators and another blower, to provide the oxygen requirements. A larger settling



basin was necessary to handle the poorer settling sludge produced with the new waste addition.

These changes were made and the plant demonstrated a capacity in excess of that designed. The waste load has been as high as 8,100 lbs. with a purification efficiency of 84%. Phenol reductions remained consistently between 92 and 96%

A typical set of analyses is as follows:

	<u>pH</u>	<u>Phenol</u>	<u>BOD</u>	<u>COD</u>	<u>Phos.</u>	<u>Nit.</u>	<u>Sett.</u> <u>Solids</u>	<u>Susp. Solids</u>	
								<u>Total</u>	<u>Volatile</u>
Feed	8.0	630	4865	7900	8.0	15.0			
Aeration Basin	7.7	25	440	1885	8.0		630	4520	4000
Final Effluent	7.6	23	430	1885	8.0	4.0	2	180	150

All values except pH in mg/l.

These two plant experiences show quite vividly that wastes considered toxic can be treated biologically and that activated sludge can function effectively.

Purification of cotton linters is one of the major processes at the Hopewell, Virginia plant. Linters are the short fibers remaining on the cotton seed after ginning. These are shaved off the seed, baled and sold as raw lint. They are basically high quality alpha cellulose but initially contain oils, hemi-celluloses, lignins, waxes, and other materials. Processing consists essentially of cooking with caustic liquor, washing, bleaching and packaging. The liquid wastes resulting are those from the cooking stage, dark brown in color, high in dissolved solids, BOD and pH, wash waters which are essentially dilute cooking liquors, and bleach waters both acid and alkaline in nature, low in BOD with some residual chlorine.

Improvement in the James River quality required a reduction in the overall plant waste load. Since linters operations produced the largest BOD load, it was felt that initial reduction should be in this area. A study program was developed to provide design criteria for a treatment plant.

The waste water to be treated had the following analyses:

pH	12.0	
MO Alk	1,700	mg/l
BOD	1,230	mg/l
COD	3,600	mg/l
Total Solids	4,700	mg/l
Volatile Solids	1,800	mg/l
Fixed Solids	2,900	mg/l
Nitrogen	30	mg/l
Phosphorus	6	mg/l
		Temp. 35-40°C

The high pH of the waste water made it advisable to study the effect of this factor on the oxygen uptake by activated sludge. Daily doses were added to an activated sludge which had been receiving domestic sewage. A well acclimatized seed was developed after pH adjustment and addition of nitrogen and phosphorus. Suitable portions of the waste were diluted to 10% and fortified with N and P. Acclimatized seed was used in the Warburg respirometer and runs made after adjustment to several pH levels. The uptake was measured at intervals up to 100 hours.

As shown in Figure 14, both the rate of intake and total uptake were much alike in the pH ranges from 7.0 to 9.0, but at 10.4 both rate and total were considerably reduced. From this, it appeared that the pH was definitely limited to not much above 9.0

Batch aeration studies were carried out using various dilutions, nitrogen and phosphorus were added and the pH adjusted to 8.0-9.0. Adapted sludge solids were added to provide a suspended solids concentration of 2,500 mg/l. The aeration period was 24 hours and samples were taken at intervals over 24 hours. As shown in Figure 15, the 10% dilution gave a much higher removal than the 20%, which in turn was better than the 30% and indicated an optimum dilution of about 10%.

Titration studies for neutralization of the waste were made and are shown in Figure 16. This shows the effect of the acid bleach liquor in reducing acid consumption.

Because of the high temperature of the waste water, Warburg studies were carried out to determine the effect of temperature on oxygen utilization. Using adapted sludges, the oxygen uptake was determined for temperatures from 25°C to 45°C. Figure 17 shows the results. For this waste water and adapted sludge, 40°C is the maximum allowable for effective treatment.

Optimum nitrogen and phosphorus concentrations were necessary in the wastes. Warburg respirometer studies were made on the oxygen uptake using adapted sludges to determine these requirements. In one set, BOD/P ratio was kept constant at 20:1 and the nitrogen varied from 0 to 100% on basis BOD:N of 20:1. In the other, the BOD/N was kept constant at 20:1 and the phosphorus varied from 0 to 100% on basis BOD:P of 20:1. This work is shown in Figure 18 (N ratio) and 19 (P ratio). The data shows BOD:N as 20:1 and BOD:P as 40:1.

With this background, aeration studies could be carried out. Eight sets of operations were made. In these, aeration time, aeration solids, pH and alkalinities were varied to develop purification efficiencies together with sludge solids concentration. Waste HCl was used for pH adjustment in this work.

Table 2 shows the data obtained. Good purification of the waste water was obtainable with an aeration period of 16 to 24 hours, and pH values in the 8 to 9 range. From this work, satisfactory purification in the 80 to 90% range could be obtained. Runs 6-7-8 show pH adjustment brought about in the aeration tank.

Full scale operation meant a population equivalent of 150,000 people (BOD loading of 25,000 lbs.) and 2.5 mgd flow. Because of the magnitude of the work, a 30 gpm pilot plant was constructed to obtain more critical data with especial reference to oxygen requirements and sludge production and handling. This plant would operate on waste water actually discharged to the river.

The plant comprised an 18 ft. diameter steel aeration tank holding 16 feet of water and equipped with a turbo aerator, air blower, final settling basin, pH corrector, sludge pumps, thickener tank and vacuum filter.

Plate 2 shows the pilot plant.

This unit was operated for 4 months with varying rates of aeration and retention, sludge solids concentration, BOD loading, sludge recycle, and vacuum filtering of the thickened sludge.

This work confirmed the semi-pilot work in optimum aeration time, sludge solids concentration and sludge production. Oxygen requirements were somewhat greater due, we believe, to the difference in aeration agitation.

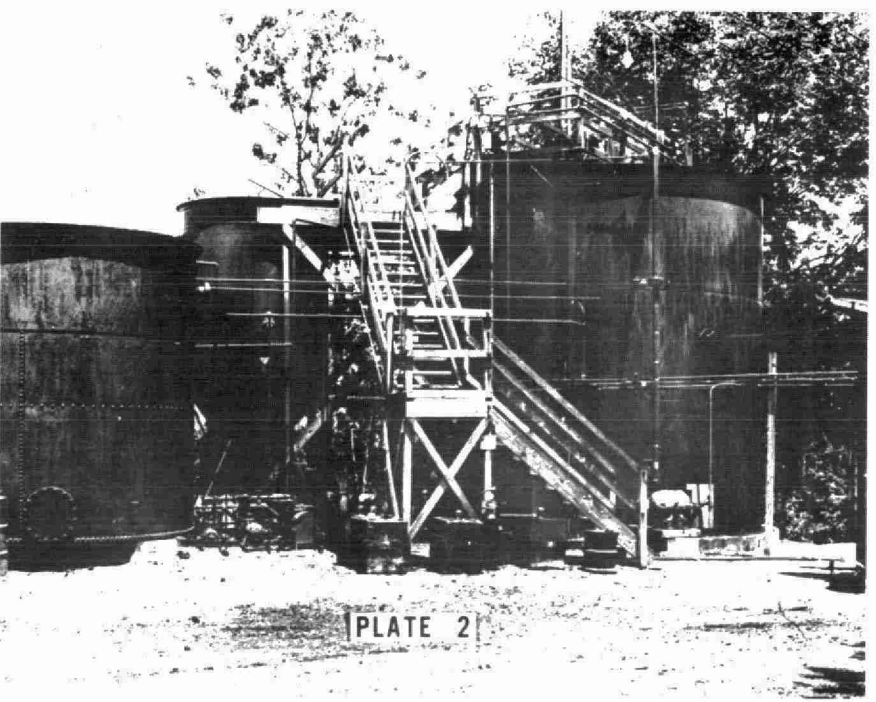
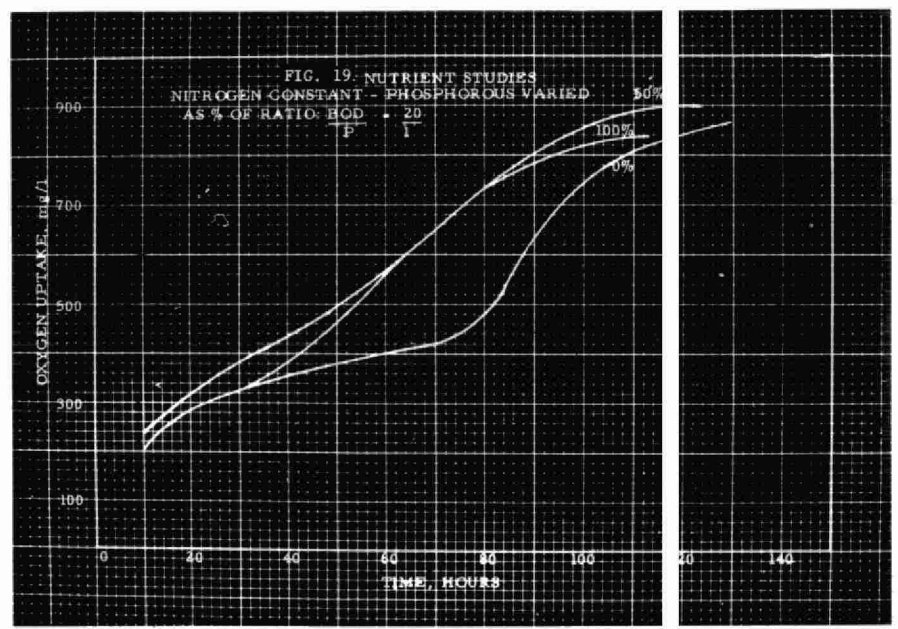
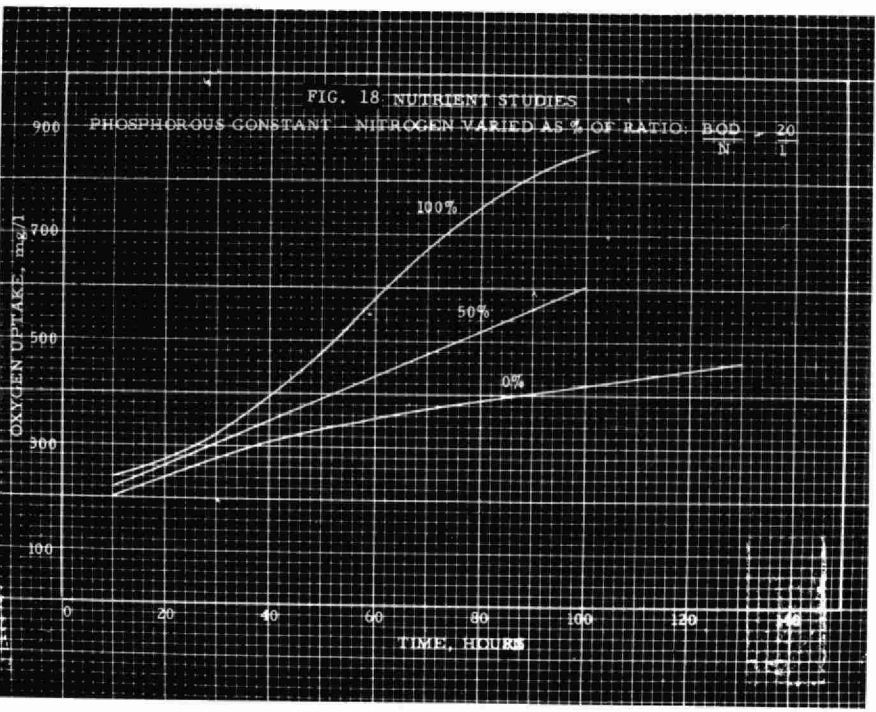


PLATE 2

TABLE 2
BIOLOGICAL TREATMENT OF COMPOSITE WASTE
Chemical Analyses

Run	Tank	Detention Time - hr.	Aeration Solids				Influent				Effluent			
			total	volatile	% vol.	SDI	BOD	COD	pH	alkalinity	BOD	COD	pH	alkalinity
1	99	24	1950	1680	86	1.25	1100	2880	7.1	366	133	1160	7.6	370
2	99A	24	2800	2400	86	-	1180	2920	8.6	490	100	1090	8.2	660
3	99B	24	4640	4070	88	0.75	1420	3910	8.9	670	104	1880	8.3	945
4	101	24	2140	1940	91	1.50	1560	3870	8.8	660	160	1840	8.4	1060
5	102	16	4740	4240	89	0.57	1100	3130	10.6	827	134	1440	8.7	1270
6	103	12	4210	3710	88	1.25	1130	-	10.7	950	180	-	8.8	1350
7	104	12	4290	3560	83	-	1210	-	11.7	1110	308	-	8.9	1550
8	105	12	4040	3230	80	-	1130	-	11.6	1320	280	-	9.1	1660

solids, BOD, COD, in milligrams per liter
alkalinity in milligrams per liter to pH 4.5, as CaCO₃
SDI - Sludge Density Index
vol. = volatile

Figure 20 shows the curve developed for oxygen required.

Figure 21 shows the effects of turbine blower ratio on oxygen transfer efficiency.

Figure 22 shows the sludge production.

With this data, the full scale plant was designed and constructed.

Plate 3 shows an aerial photograph of this plant.

The system comprised pH correction, using waste HCl, an equalization basin holding 24MG; this was necessary due to a 10-day on and 4-day off process schedule and a two week vacation downtime, an aeration basin of 2 MG capacity, a final basin 80 feet diameter providing 3 hours retention, sludge thickener, sludge storage tank and vacuum filtering equipment, together with necessary transfer pumps, aqueous ammonia and phosphoric acid storage tanks and feed pumps.

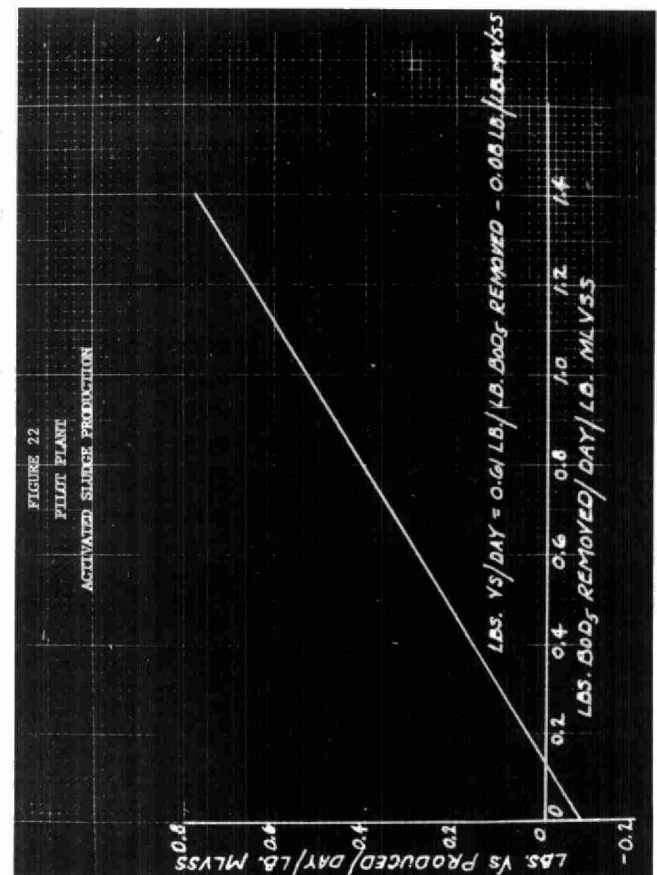
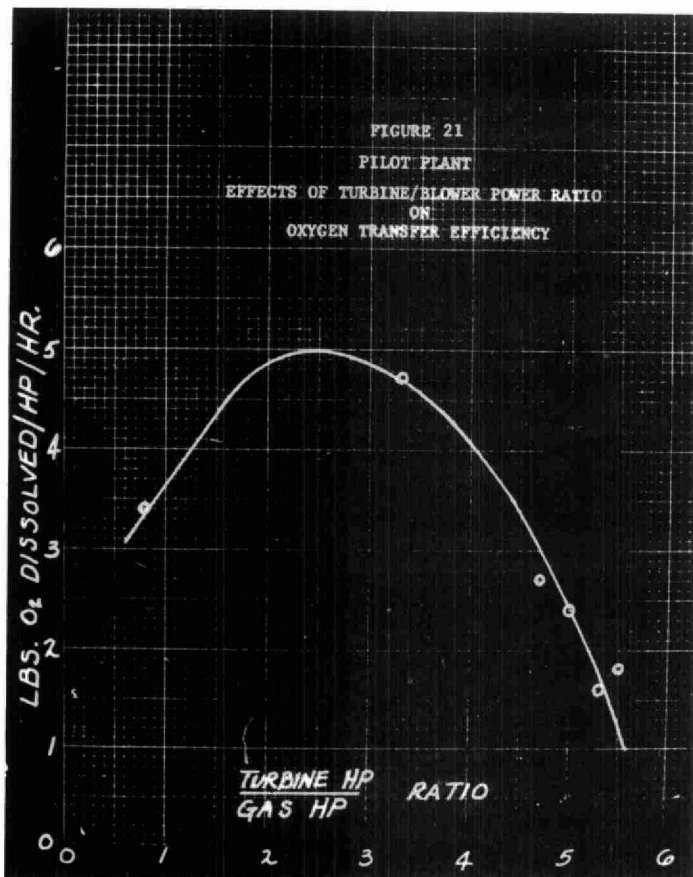
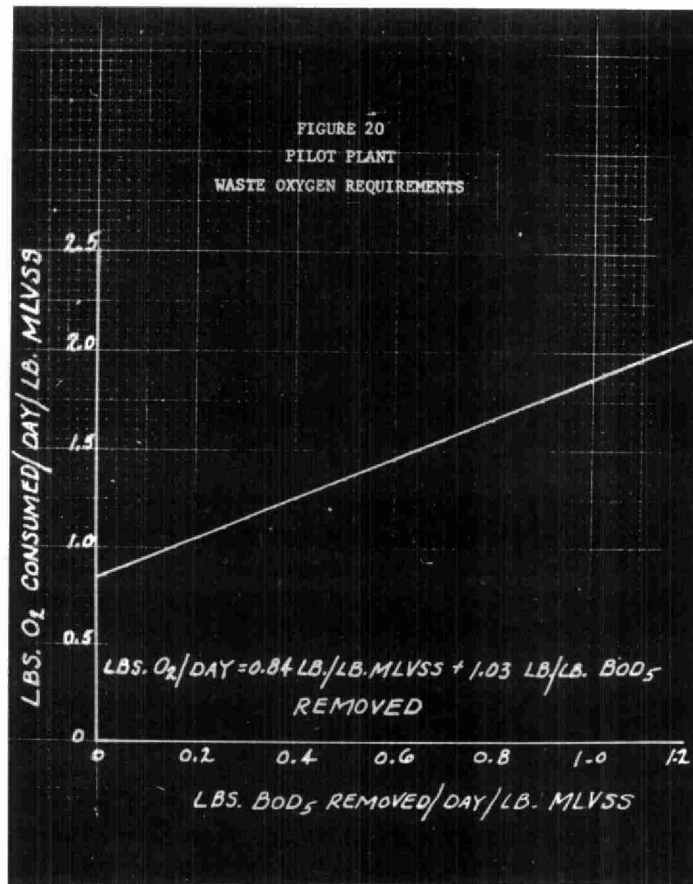
The aeration basin was provided with two 3,000 cfm air blowers with 100 HP motors and two 250 HP turbo aerators.

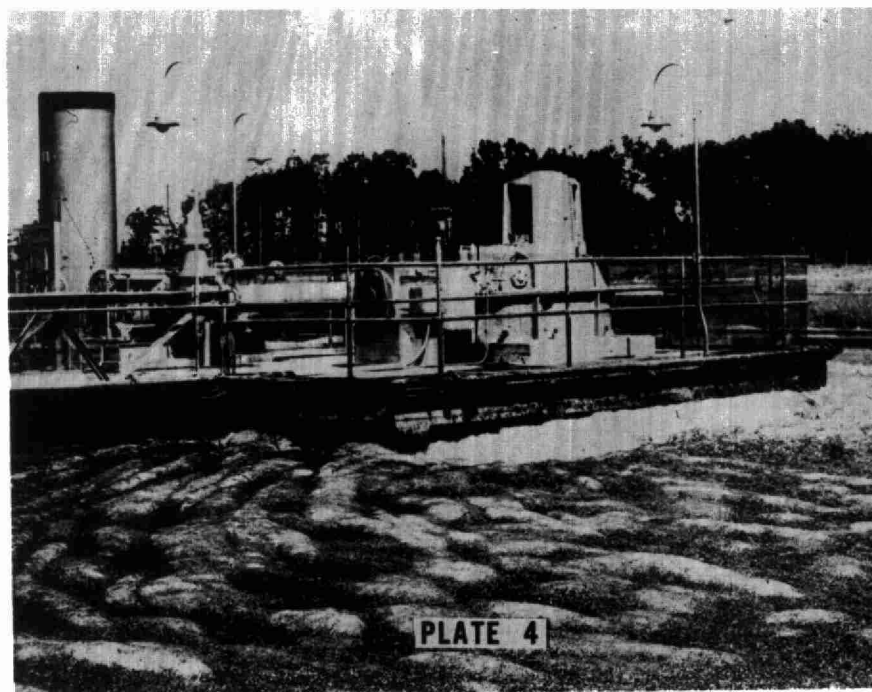
Plate 4 shows the aeration basin with blowers and turbo aerators.

The system was placed in operation by seeding the aeration basin with fermented waste white water sludge and gradually applying the waste water feed. Building up to a full load took somewhat over 30 days. Excellent purification was obtained.

The plant has consistently provided 90%+ efficiencies, reducing the 1100 to 1210 influent BOD down to 50 to 80 mg/l. Suspended solids in the mixed liquor average around 4,000 mg/l. Sludge density index has been around 1.3. The turbo aerators have given excellent performance, the oxygen transfer efficiency being about 40%.

In conclusion, activated sludge can be a most effective method of treating waste waters from chemical operations. The design must be the result of careful and thorough laboratory, semi-pilot and possible pilot plant studies. With this phase carefully performed, the final plant will be one that can and will function in a satisfactory and economical manner.







"WASTE CHARACTERISTICS AT URANIUM MILLS
AND ASSOCIATED ENVIRONMENTAL ASPECTS"

by

S. D. SHEARER

INTRODUCTION

The U. S. Public Health Service has conducted since 1957 detailed in-plant surveys at American uranium mills. These surveys have been made at plants that use various uranium extraction processes. The plants studied were selected on the basis of providing a representative cross section of all extraction processes now being used in the United States. The objectives of these surveys have been several: (1) Characterize the liquid and solid wastes produced in the processing of uranium ore, (2) determine the effectiveness of waste control measures practiced at the various uranium mills, (3) arrive at effective means of reducing radioactive and chemical discharges to the environment, and (4) study the pollutional effects of mill discharges on the water environment and the public health implications of these discharges.

These studies have yielded considerable information about the milling process and the kinds of wastes and characteristics to be expected from the various extraction processes.

Detailed environmental surveys have been conducted near American uranium mills to determine: (1) The effects of waste discharges upon various water uses, (2) the pathway by which radioactive materials move in the water environment, and (3) a precise relationship between natural background radioactivity levels and radioactivity levels reflecting man-made waste discharges.

Laboratory research studies have also been conducted on the mechanism influencing leachability of radium-226 from river sediments and uranium mill waste tailings.

The purposes of this paper are to present some of the highlights from the above-mentioned studies and some additional recently developed information. Considerably more details on this subject can be found in References 1 through 6.

SCOPE OF U. S. URANIUM ACTIVITIES

The majority of United States uranium mining and milling is centered primarily in the western United States and predominantly in the Colorado Plateau area.

Table 1 lists the operating uranium mills as well as the inactive uranium mills in the United States. A total of approximately 18,365 tons of ore per day are milled at presently operating uranium mills. In 1961 this total was approximately 23,000 tons per day. The decrease has been primarily due to curtailment of uranium procurement by the U. S. Atomic Energy Commission. There are at present 11 inactive uranium mills, and 7 of these are in the Colorado River Basin.

TABLE 1

Uranium Processing Mills^{1,7}

Company	Location of mill	Design ore capacity, T/day	Estimated cost of mill, \$
<u>Operating Mills</u>			
American Metal Climax, Inc.	Grand Junction, Colorado	330	3,088,000
Anaconda Company	Grants, New Mexico	3,000	19,358,000
Atlas Corporation	Moab, Utah	1,500	11,172,000
Atlas Corporation	Mexican Hat, Utah	1,000	11,172,000
Cotter Corporation	Canon City, Colorado	200	1,800,000

Company	Location of mill	Design ore capacity, T/day	Estimated cost of mill, \$
Dawn Mining Company	Ford, Washington	400	3,100,000
El Paso Natural Gas Co.	Tuba City, Arizona	300	3,600,000
Federal-Radorock-Gas Hills Partners	Fremont County, Wyoming	520	3,370,000
Globe Mining Company	Natrona County, Wyoming	490	3,100,000
Homestake-Sapin Partners	Grants, New Mexico	1,500	9,000,000
Kermac Nuclear Fuels Corp.	Grants, New Mexico	3,300	16,000,000
Mines Development, Inc.	Edgemont, South Dakota	400	1,800,000
Petrotomics Company	Carbon County, Wyoming	200	1,500,000
Susquehanna-Western Inc.	Falls, City, Texas	200	2,000,000
Union Carbide Corp. Nuclear Division	Maybell, Colorado	300	2,208,000
Union Carbide Corp. Nuclear Division	Rifle, Colorado	1,000	8,500,000
Union Carbide Corp. Nuclear Division	Uravan, Colorado	1,000	5,000,000
Utah Construction and Mining Company	Fremont County,	980	6,900,000
Vanadium Corporation of America	Shiprock, New Mexico	300	3,161,000
Vitro Chemical Company	Salt Lake City, Utah	600	5,500,000

Company	Location of mill	Design ore capacity, T/day	Estimated cost of mill, \$
Western Nuclear, Inc.	Jeffrey City, Wyoming	845	4,300,000
		<hr/> 18,365	

Inactive Mills

Union Carbide Corp. Nuclear Division	Rifle, Colorado
Kermac Nuclear Fuels Corp.	Gunnison, Colorado
Susquehanna-Western, Inc.	Riverton, Wyoming
Homestake-New Mexico Partners	Grants, New Mexico
Lakeview Mining Company	Lakeview, Oregon
United Nuclear Corporation	Grants, New Mexico
Vanadium Corporation of America	Durango, Colorado
Vanadium Corporation of America	Hite, Utah
Vanadium Corporation of America	Naturita, Colorado
Union Carbide Corp. Nuclear Division	Green River, Utah
Union Carbide Corp. Nuclear Division	Slick Rock, Colorado

During calendar year 1963 the U. S. Atomic Energy Commission procured 14,218 tons of uranium concentrate (U_3O_8) from United States producers.⁷ This amount represented 62 per cent of the total United States U_3O_8 procurement. Table 2 below presents a list of countries from which uranium concentrate was purchased.

TABLE 2

U. S. Atomic Energy Commission
Uranium Procurement - 1963

Country	U_3O_8 tons	% of Total
USA	14,218	62
Canada	4,651	20
South Africa	4,134	18
Australia	17	0
Total	23,020	100

MILLING PROCESSES AND WASTE CHARACTERISTICS

Raw Material

The uranium-bearing ore material milled at American mills contains generally 0.1 to 0.3 per cent uranium as the oxide (U_3O_8). This means that each ton of raw ore contains 2 to 6 pounds of uranium. The natural uranium present in the ore is made up of both uranium-238 and uranium-235. Both these isotopes of uranium are parents of natural radioactive decay series. Uranium-238 is normally present in the ore to the extent of 99.28 per cent with uranium-235 accounting for 0.71 per cent. The uranium-238 decay series is therefore the one of most importance. This series is shown as Figure 1.

URANIUM - RADIUM FAMILY

(MINOR BRANCHES NOT SHOWN)

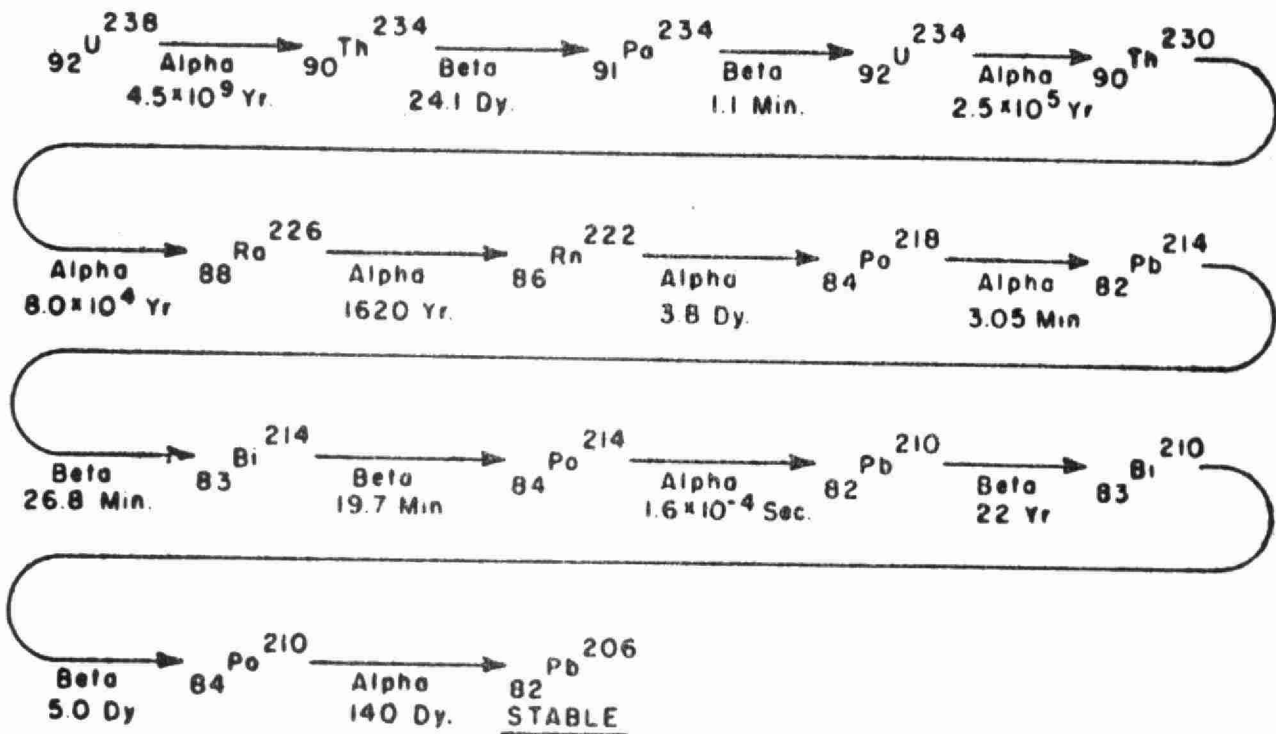


Figure 1

Most uranium ores contain this family of elements in secular equilibrium. This means that the daughter products of uranium-238 are being formed at the same rate they are decaying, with the amount of any member of the chain remaining constant. Some selective leaching occurs to upset this secular equilibrium, and though this condition is not uncommon, the ores encountered in our studies were essentially at secular equilibrium.

Assuming secular equilibrium conditions, calculations show a total radioactivity of 2.1 millicuries for each pound of uranium in the raw ore. Of the total radioactivity delivered to a uranium mill in the raw ore, 15 per cent ends up in the uranium product and 85 per cent remains behind as waste.

In 1961 a total of 200 curies per day were delivered to American uranium mills in the raw ore. Thirty curies per day went out as uranium concentrate with 170 curies per day remaining behind as liquid and solid wastes. These wastes constitute the major disposal problem of the uranium industry.

Milling Processes

Due to the differences in the natural characteristics of uranium ore, the processes used vary considerably among the different uranium mills.

In general, the four basic steps in the milling of uranium consist of crushing, grinding, uranium leaching, and uranium recovery. Crushing and grinding operations are basic to all processes and are generally the same at all uranium mills. Uranium leaching and recovery vary depending upon the particular type of ore being milled.

The uranium ore usually arrives at the mill by truck from the mines. In many instances the mills are located some distance from the mines, and trucking distances of 50 to 300 miles are not uncommon; in other instances trucking distances are only several miles.

Upon receipt of the ore at the mill it is weighed and its moisture content is determined. The ore is then crushed and ground to a very fine particle size. During these operations a representative sample of the incoming ore (usually 0.10 per cent or 2 pounds per ton) is collected. This sample is assayed for its uranium content and is the basis for payment to the mine. Depending upon the physical

layout of the mill the ground ore is either stored in large bins or fed directly to the mill process.

The ground ore is next slurried with water or recycled mill solution and the uranium extracted by two basic processes:

- (1) Acid leaching with sulphuric acid, which is usually done at a pH around 1.0, with leaching times generally exceeding 12 hours. In some instances heating is employed to facilitate uranium leaching.
- (2) Alkaline leaching with carbonates, which is usually performed on ores exhibiting a relatively high lime content. This process is almost always carried out at comparatively high temperatures (250°F), and pressure vessels are commonly used. Total leaching time ranges from 10 to 72 hours.

The next step in the process is separation of the spent ore solids from the leach solutions containing the dissolved uranium. This is accomplished by three main methods: (1) Sand-slime separations, (2) countercurrent decantation washing in classifiers and thickeners, and (3) filtration. The method used depends exclusively on the leaching process. In alkaline leaching processes, spent ore solids are usually separated by multiple-type filtration. In acid leaching processes, the spent ore solids are separated by countercurrent decantation measures, the sands being removed first by classifiers, and the slimes being removed by thickening processes.

The next process step involves the recovery of dissolved uranium from the leaching solutions. Here again the method used depends on the leaching process. The simplest method for recovery of dissolved uranium is by direct chemical precipitation. This is usually carried out only on alkaline leach liquors, which is feasible because alkaline leaching dissolves very little material from the ore except uranium.

Acid leach liquors are quite different from alkaline leach liquors. The acid leaching process dissolves a number of impurities from the uranium ore, and these impurities interfere with the recovery of uranium. To produce a high-grade product it is necessary, therefore, to use selective ion exchange or solvent extraction methods.

Ion exchange methods have the distinct advantage of providing a relatively high uranium recovery from ores with a relatively low uranium content. This process uses certain types of anionic resins for the selective adsorption of uranium from a leach solution and usually employs two different methods: column ion exchange and resin-in-pulp (RIP). When column exchange methods are used, the pregnant acid solutions are passed through columns or beds containing the ion exchange resins. With these methods it is necessary to use only clarified solutions. The RIP method, a more recent innovation, is designed for uranium extraction from leach pulp without prior clarification of the pulp. In this process leach pulp is usually passed countercurrently through baskets or screens containing exchange resins that oscillate up and down through the leach pulp.

The solvent extraction procedures provide a highly efficient means for uranium extraction. The dissolved uranium in the acid leach liquors is transferred from this aqueous phase into an organic phase. The solvent most commonly used is tributylphosphate (TBP) in a kerosene diluent. After the transfer of uranium into the solvent, the solvent is contacted with a second aqueous solution, which alters the form of uranium so that it preferentially transfers back to the aqueous phase. This second aqueous solution is usually sodium carbonate and acidic chloride or nitrate solutions, depending upon the particular solvent being used.

The final step in the milling of uranium is to precipitate the uranium chemically from the pregnant solutions. The precipitated uranium is generally filtered, heat dried, ground, and placed in small barrels for shipment to the U. S. Atomic Energy Commission.

Waste Characteristics

As can be easily visualized from the above discussion, a wide variety of chemical and radioactive wastes is produced at uranium mills. These wastes, if indiscriminately discharged to the water environment, can be detrimental to most water uses.

To characterize the wastes properly, the in-plant surveys that have been made have necessarily been fairly extensive and sufficiently prolonged to yield useful results. These surveys have been conducted and planned with several goals in mind: (1) determination of a materials balance throughout the milling process, (2) establishment of the

qualitative and quantitative nature of waste sources,
(3) estimation of possible environmental effects, and
(4) acquisition of information to aid in improved waste management practices inside the mill processing.

Basically, the in-plant surveys have been conducted in the following manner: Detailed process diagrams were prepared giving waste flows, kinds and amounts of chemicals added at various points in the process, and other pertinent information. Next, a detailed sampling program was carried out over periods extending from 2 to 5 days. A number of representative locations were sampled throughout the mill process from entrance of raw ore in the mill to the final waste effluent streams. The samples were then analyzed for their liquid, solids, chemical, and radiological contents. The laboratory analyses, combined with desk computations, yielded information by which material balances could be made throughout the milling process. Good results have been obtained from all the in-plant surveys. Without going into great detail the following summary of waste characteristics can be presented for U. S. uranium mills.

Radium. Table 3 summarizes the amounts of dissolved radium-226 in various milling processes. Acid leaching dissolves only about 0.5 per cent of the radium-226 originally in the raw ore. Alkaline leaching on the other hand dissolves about four times as much radium-226.

In a solvent extraction circuit 5 per cent of the dissolved radium in the leach liquors leaves the mill in the yellowcake product. The remaining dissolved radium is present in the mill tailings flow. For RIP processes slightly more radium leaves the mill in the product than leaves in other exchange processes.

All the dissolved radium in alkaline leach liquors leaves the mill in the yellowcake product. When it is necessary first to concentrate the uranium in alkaline leach liquors by ion exchange or solvent extraction methods, it would be expected that the dissolved radium-226 would follow a path similar to that found for acid leach liquors.

As an example, the information in Table 3 can be used to estimate the amount of dissolved radium to be expected in the waste discharge from a particular mill. An acid leach solvent extraction mill processing 1,000 tons per day of 6-pound ore (0.3% U_3O_8) would have a radium input of 765 milligrams per day if the ore is in secular equilibrium ($85\% U/U_3O_8 \times 6 \text{ lb } U/\text{ton} \times 1,000 \text{ tons/day} \times 0.150 \text{ mg Ra/lb } U$). About 3 to 5.5 milligrams would be dissolved during leaching, 80 per cent of which would be discharged in the organic raffinate and 15 per cent with the sands and the slimes.

TABLE 3

Dissolved Radium 226 in
Uranium Mill Process Flows

Process	Total Radium dis- solved by leaching, %	Dissolved Radium leaving mill, %	
		In tailings flow	In yellowcake
Acid leach	0.4 to 0.7		
Solvent extraction			
Raffinate		(80)	
Sands and slimes		(15)	
		<hr/> 95	5
Resin-in-pulp		93	7
Alkaline leach	1.5 to 2.2		100

It is therefore, clear that the major portion of the radium input to the mill remains undissolved through the milling process and is discharged to the waste tailings piles.

Gross Alpha Radioactivity. Similar mill balances were attempted for gross alpha activity. Because of uncontrollable laboratory techniques in the preparation of samples for analysis, the amount of radioactivity detected in samples of ground ore was usually about 10 per cent less than the amount that would have been present under secular-equilibrium conditions. Of the total gross alpha activity in mill wastes, 2 to 7 per cent was in dissolved form at acid leach mills and 0.5 per cent at mills using alkaline leaching.

Waste Volume. The quantities of waste liquids produced by milling operations vary considerably depending upon the type of process used. In general, it was found

that mills using an acid leach process had a water consumption about three to four times that of mills using alkaline leaching. Waste volumes produced at acid leach mills averaged 850 gallons per ton and ranged from 538 to 1,210 gallons per ton. Waste volumes from alkaline leach mills averaged 250 gallons per ton, ranging from 81 to 403 gallons per ton.

Chemical Characteristics. Chemical characteristics of mill waste flows depend primarily upon the process used. The character of the raw ore may also influence the chemical characteristics of waste flows. For example, raw ore may contain elements such as boron, selenium, lead, fluorine, arsenic, vanadium, and others. Table 4 summarized the chemical characteristics normally found.

Alkaline leach mill wastes most usually have a pH near 10 and relatively high total alkalinity. Sodium ion concentrations are comparatively high because of large uses of sodium carbonate and sodium hydroxide. Chemical oxidants may also be present.

Acid leach mill wastes have a pH near 1 with a very high sulphate concentration. When ion exchange processes are used, the waste flows contain either nitrate or chloride ions in comparatively large quantities.

Of particular interest in waste flows is the organic solvent used in solvent extraction processes. As much as 1 to 2 pounds of organic solvent per ton of ore processed may be discharged to wastes. These organic solvents are toxic to aquatic life and if discharged to receiving streams at low-flow periods will completely eliminate stream life for long distances below mill effluent.

Waste Ore Tailings. As stated earlier, about 99.7 per cent of the ore delivered to the mill leaves as spent ore solids (or tailings). These tailings are generally slurried with water and pumped to large piles for storage. The water used for slurrying is either discharged as mill effluent or is recycled back to the mill process.

These tailings solids contain the bulk of the radium-226 that enters the mill in the raw ore because of the relatively small amounts of radium dissolved during the

Chemical Characteristics of Mill Effluents as Discharged to Tails, ppm

Table 4

Alkaline leach mills					Acid leach mills						Solvent extraction	
					Resin-in-pulp			Solvent				
					a	Sands only	Slimes only ^a	Alkyl-amine	EH ₁ A	Amine + TBP ^b		
Cl	358	275	286	81	190		240	205	110	35	3740	
SO ₄	2460	-	-	1760	3860	2210	2180	2330	2910	11,000	7500	
Mg	-	-	-	10	535	42	120	75	72	-	-	
NO ₃	73	-	-	-	1270	2680	0	2230	-	-	-	
Cu	0.005	-	-	-	1.3	< 1.0	-	-	-	0.2	1.6	
Be	-	-	-	-	-	-	-	-	-	2.2	0.8	
Fe	0.52	-	-	0.1	42.0	0.1	-	0.14	220	57.0	5.4	
Mn	< 0.15	-	-	-	110.0	-	7.0	-	30	11.0	9.1	
Pb	-	-	-	-	0.65	0.4	-	-	-	-	-	
As	< 0.01	0.20	0.49	-	0.21	< 0.01	-	-	-	14.5	4.9	
B	-	-	-	-	0.1	0.2	-	-	-	-	-	
U	5.6	-	-	-	2.9	0.25	-	-	-	-	-	
Na	-	2950	-	3450	-	910	-	-	-	-	34.0	
Ca	-	-	-	< 10	530	815	570	730	520	1055	5400	
HCO ₃	-	-	-	1100	-	-	-	-	-	-	-	
CO ₃	-	-	-	4610	-	-	-	-	-	-	-	
F	2.0	-	-	-	-	1.2	-	-	3.8	13.0	8.0	
V	-	-	-	-	-	-	-	-	-	0.04	34.0	
TDS	7830	-	-	8270	7360	6410	-	-	4370	-	19,300	
Total alka-												
linity	1860	4050	3560	-			-	-	-	-	-	
pH	10.0	9.6	-	10.8	3.3	7.7	-	-	2.6	2.1	2.1-4.1	

^a After neutralization.

^b Effluents from tails, weighted average

mill process. Consequently, these materials have a very high radium-226 content per gram. As an example, Table 5 presents the variation in radium content per gram for a representative tailings sample collected at an acid leach solvent extraction mill. The very finest particle sizes contain the highest radium content per gram. These size solids are also the hardest to control and eliminate from effluents discharged to receiving bodies of water.

TABLE 5

Particle Size and Radium Content of Waste Ore Tailings
Acid-Leach Solvent Extraction Process

Sieve No.	Size of opening, u	Radium-226, uug/g dry weight
20	840	396
30	590	358
50	297	173
60	250	137
70	210	128
80	177	165
100	149	182
120	125	277
140	105	343
Pan	< 105	972

WASTE CONTROL MEASURES

Reduction of Settleable Solids

Because of the nature of waste produced in milling operations it is necessary to make a concerted effort to develop control measures at the waste source in order to adequately protect water uses downstream from mill discharges. Methods should be developed to reduce both radiological and chemical effects of the waste.

Waste treatment and control practices at U.S. uranium mills have greatly improved during the last 5 years. At present there are only one or two isolated locations where high concentrations of radioactive and chemical wastes are discharged directly to streams. In these two cases various waste control measures are under investigation by the mills concerned.

One of the simplest means and a basic minimum form of treatment is the use of mill tailings piles. This measure is of real value in preventing many potential damages to water uses. With adequately constructed tailings ponds or lagoons it is possible to eliminate essentially all settleable waste solids from mill effluents, which consequently reduces the total amount of radium entering the surface watercourses. In addition to controlling solid discharges to the stream, tailings ponds or lagoons can serve as reservoirs for evaporation of the associated liquids, or the liquids can be recycled back to the mill process. The amount of overflow from tailings ponds depends essentially on the amount of liquid input and the amounts of evaporation and seepage that occur. Sometimes there is no pond overflow because of comparatively high evaporation rates. One uranium mill is located so close to the mines that waste ore tailings are merely slurried with water and pumped back into the mined-out areas of the uranium mine.

As a guide to the proper construction of such retention systems, the U. S. Public Health Service and the U. S. Atomic Energy Commission together have recently developed an AEC licensing guide and evaluation of embankment retention systems.⁸

One of the major problems with respect to waste ore tailings is ultimate disposal. When a mill is closed down, the waste ore tailings are left behind because they do not contain sufficient uranium or other materials to warrant recovery. The Public Health Service and Atomic Energy Commission are making a complete study of potential hazards associated with abandoned tailings ponds and of ultimate disposal of these tailings.

Reduction of Dissolved Constituents

Neutralization of acid or alkaline mill wastes reduces significantly the concentration of many dissolved pollutants. Dissolved radium-226 in acid mill wastes can be reduced by 90 per cent through neutralization, and thorium isotope concentrations can be reduced to negligible amounts. Some reduction in the dissolved lead-210 content can be expected also. Neutralization of acid wastes brings about the precipitation of several chemical components often present at undesirably high concentrations, such as iron, lead, arsenic, copper, manganese and magnesium; the harmful effects of excess acidity on the aquatic life of a receiving stream are, of course, eliminated by this treatment step.

Reduction in dissolved radium-226 concentrations may be required beyond that obtained by neutralization, and this can be accomplished by treatment of the neutralized mill waste with barium compounds. The liquid waste may be percolated through a column or bed of barite, the crude mineral form of barium sulphate, or treated in agitated tanks by the addition of refined chemical forms such as barium chloride or barium carbonate as well as barite. Radium removal efficiencies of up to 90 per cent have been obtained in laboratory tests of barium treatment and plant scale testing at some mills.

Raffinate waste from the solvent extraction process, which has been noted to be very toxic to aquatic life, is commonly stored in ponds designed for evaporation and seepage sufficient to prevent any overflow. Before entering the ponds the raffinate passes through stilling tanks where any heavy excess of solvent may be skimmed from the surface and reused in the extraction process. Since harmful concentrations of solvent will remain entrained in the raffinate, additional treatment would be required at this point before discharge to a stream.

The final disposal of liquid mill wastes by deep-well injection has been applied at an acid leach-RIP mill with apparent success. This acid waste is first settled, treated with copper sulphate for slime control and a sequestering agent, then filtered before being added to the well. As the treated waste water enters the

porous formation at a depth of 1,000 feet below the ground surface, neutralization, precipitation, and ion exchange with the underground sands occur. The useful life of this well is estimated to be 10 years based on the porosity and ion exchange capacity of the disposal formation. Great care is, of course, necessary with such a system to ensure that useful aquifers do not become contaminated.

ENVIRONMENTAL ASPECTS OF MILL EFFLUENT DISPOSAL

The U. S. Public Health Service, in connection with in-plant studies mentioned above, has also conducted numerous stream investigations concerning the environmental aspects of waste discharge from uranium mills. Most of these studies have been special short-term investigations. At present, however, a long-term, continuous monitoring program for a continuing check of the effects of uranium milling waste discharges is being carried out as part of the activities of the Colorado River Basin Water Quality Control Project of the Public Health Service.

In all these studies radioactivity derived from mill operations has been detected in every environmental sample collected below mill discharges, including river waters, bottom sediments, fish and other aquatic life, farm topsoils, crops and vegetables, and milk.

To give an idea of radioactivity levels found in the water environment in the western United States a comparison will be made between the levels found prior to extensive waste treatment practices and the present levels.

The natural or background concentration of dissolved radium-226 in surface waters of the western United States has proved in the majority of cases to be less than 0.1 micromicrocuries per litre with a small fraction of the results ranging up to 0.2 or 0.3 micromicrocuries per litre. The natural gross alpha radioactivity of these surface waters does not often range above 10 micromicrocuries per litre. The observed natural uranium content has averaged about 3 micrograms per litre and has ranged as high as 8 or 10 micrograms per litre. The very small number of samples analyzed thus far for lead-210 indicates a natural

concentration of less than 0.10 or 0.20 micromicrocuries per litre.

Sediment samples at uncontaminated locations in the western United States have shown average radium-226 concentrations of 1 to 2 micromicrocuries per gram and gross alpha concentrations of about 10 to 15 micromicrocuries per gram.

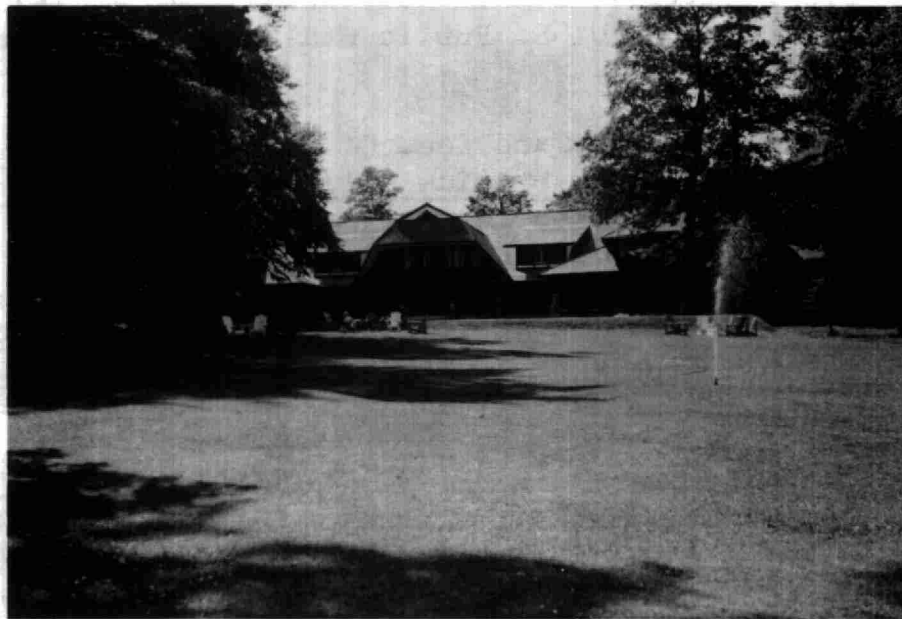
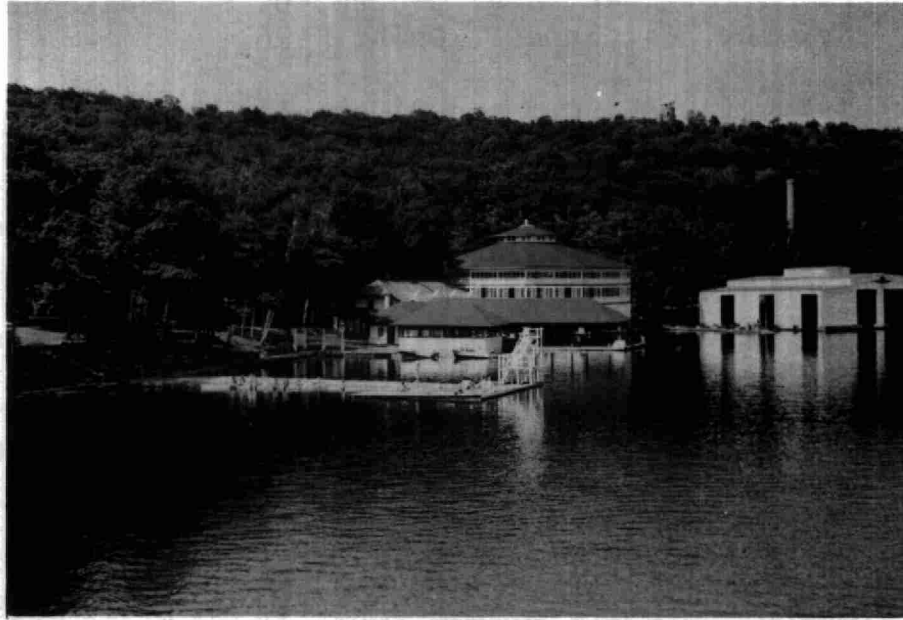
In contrast to the above figures, water and sediment samples collected downstream from uranium mill discharges, prior to extensive waste treatment measures by the uranium mills, have shown dissolved radium-226 concentrations as high as 88 micromicrograms per litre and sediment concentrations of radium-226 as high as 730 micromicrograms per gram. Gross alpha radioactivity of these waters ranged as high as 2,000 micromicrocuries per litre for waters and as high as 10,000 micromicrocuries per gram for sediments.

At the present time the highest average radium-226 concentration in surface waters of the Colorado River Basin below uranium mills is 1.1 micromicrograms per litre. (This can be compared with the U. S. Public Health Service drinking water standards for radium-226 of 3.0 micromicrograms per litre.) At this same location radium-226 content of sediments averages 4.5 micromicrograms per gram.

In conclusion it is seen that, while in early years of uranium mining in the western United States very high contamination levels were found in the water environment, concerted effort on the part of the industry in the development of adequate waste treatment methods has resulted in drastically reduced concentrations.

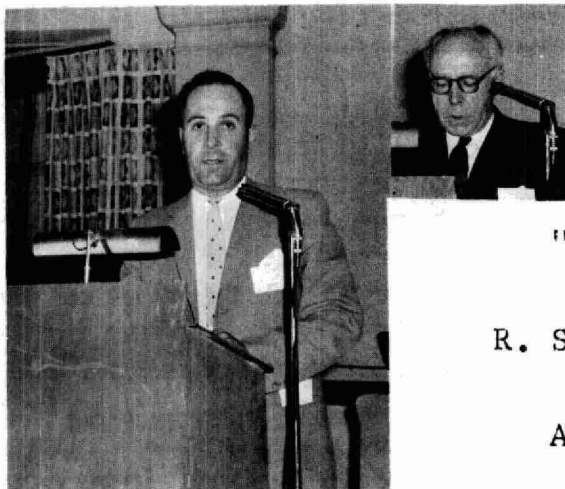
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BIGWIN INN

SESSION TWO



K. M. Mayall

Dept. of Energy & Resources Management
Conservation Authorities Branch

Session Chairman

"CHROMATE TOXICITY"

by

R. S. INGOLS, R. H. FETNER

and

A. B. ESCHENBRENNER

Paper delivered by
F. A. Voegelé, Director
of OWRC Laboratories

The toxicity of chromates has claimed some attention in the last ten years because the information has not been wholly consistent. The results of studies of fish toxicities show a 24-hour median tolerance limit of 300 mg/l of chromates which is a thousand fold greater than that of mercury (6). Similarly, R. D. MacKenzie, C. A. Hoppert, and R. U. Byerrum (8) found that there is very little retention of chromate by mice when fed in drinking water at low concentrations (1 mg/l) and no evidence of pathology at any concentration studied. In similar studies with dogs and rats, C. L. Decker, C. A. Hoppert, and R. U. Byerrum (1) found no pathology from chromates. In BOD tests a committee of the Federation (3) determined that the median tolerance limit of 10 mg/l of chromates is a thousand fold greater than that of mercury, which is known to have a high acute toxicity.

After considering these results, it would seem that the tolerance limit for chromates in drinking water is defined by the United States Public Health Service for interstate carriers (9) could easily have been raised from 0.05 mg/l to 1.0 mg/l or even more in 1962. In fact, discussions with Public Health Service

Personnel indicated that on Long Island the examination of a family which had been drinking well water with high chromates (25 mg/l) showed no deleterious response.

There is other evidence, however, of a very different sort. The respiration rate of a mass of bacteria is not affected by 1 mg/l of chromate, but only a small portion of them can reproduce in ordinary media after 6 hours contact with the 1 mg/l chromate solution (5). Bacteria cannot reproduce, or at least cannot develop visible colonies, on a nutrient agar plate containing 500 mg/l chromate, while slower growing molds with two sets of chromosomes can grow. Because of these observations by two of the authors, some rapidly growing (reproducing) insect egg cells were placed in a dilute chromate solution for 16 hours. Observations indicated that many cells began the process of cell division but could not complete the process (4). These cells suffered from chromosome aberrations. Cells with certain aberrations will eventually die because the nucleus is so severely damaged that the reproduction process can not be completed. The cell with such a damaged nucleus, however, can still respire for several hours (3-5 times the normal time between divisions) even though it cannot complete the reproduction cycle (or process). This ability to respire, and inability to reproduce, parallels the bacterial observations but the chromosome aberrations lead to a much more significant consideration. Cancer cells have an abnormal number of chromosomes. Many environmental factors which cause chromosome aberrations also lead to cancers. The most notable such environmental factor is radiation.

Industrial hygiene reports (2) indicate that workers who handle chromates have a much higher incidence of lung cancer than workers in other chemical factories. Here, however, it is obvious that chromate dust may have been carried into the lungs during respiration. In the metal plating industry, chromates are heated on an open hearth; some workers who breathe the fumes develop lesions in which the flesh of the nose and jaw disappears. This pattern is very similar to those lesions seen in people

with a high radium concentration in the mouth zone. Again, the flesh has been affected by chromate which has fallen directly on the flesh.

While it is not too difficult to see how chromate particles can develop lesions of the flesh where they fall, it is much more difficult to see how a chromate molecule in solution in drinking water can pass unaltered through the stomach wall into the blood stream and from there to some cell to cause the chromosone aberration pattern which can then develop into a cancer. Observations on the chromate-fed dogs (1) did state, however, that some hexavalent chromium, chromate, was deposited in certain organs.

To test the possibility that orally ingested chromates can produce cancer, 50 mice were obtained for a test. These mice were chosen because one of the co-authors knew that this strain of mice commonly develops lung tumors in a predictable number in 8 months. When a group of this strain of mice is irradiated, the number of lung tumors is increased. The 50 mice were evenly divided, the 25 controls were fed an optimum diet and tap water, the second 25 mice were fed the same food, but their water was dosed, or polluted, with 1 mg/1 sodium chromate.

Before the end of the test 10 of each of the animals had been lost. At the end of the 8-month test period the lungs of each animal were removed, and examined for tumors. Two lung tumors were found in the 15 controls; eight lung tumors were found in those 15 animals drinking water with 1 mg/1 chromate.

Are these results in conflict with the negative observations with dogs and men with chromates in their drinking water? The authors believe not; there were, also, seven chromate treated mice whose lungs showed no obvious tumors. It is admitted that even the positive results are not statistically significant.

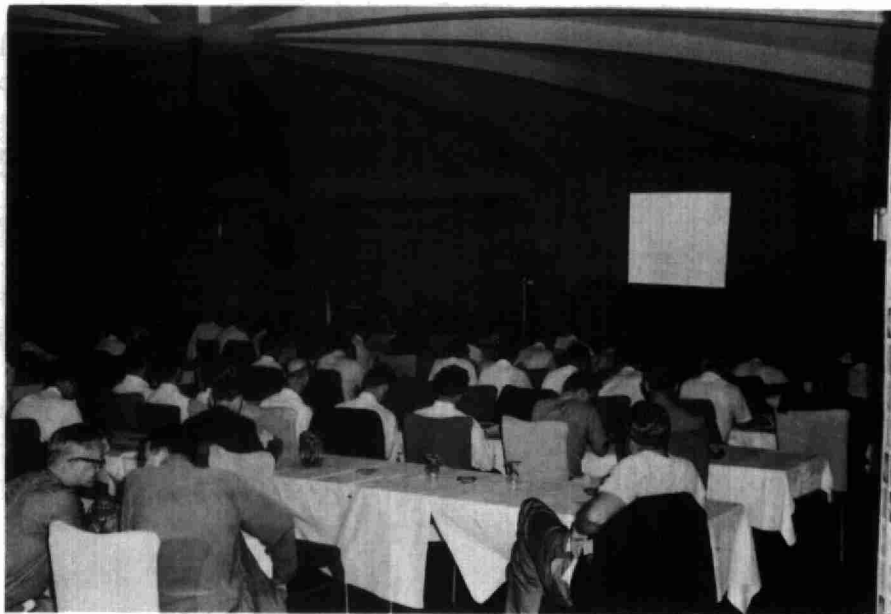
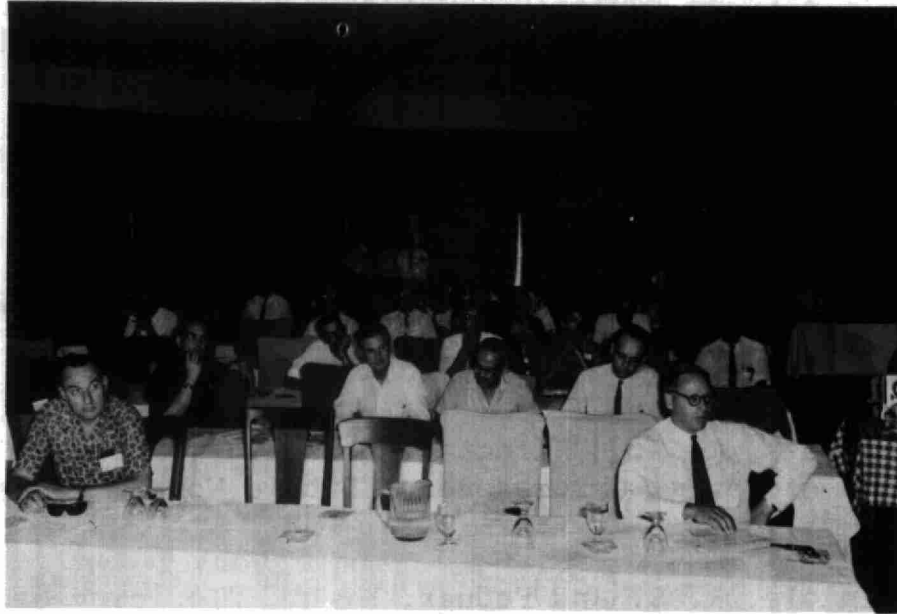
We conclude, however, that chromates in drinking water can increase the number of lung tumors in tumor-prone mice. We do not know whether more chromates will

increase the incidence of tumors or whether the results of this experiment can even be repeated. However, the very preliminary results, as well as other data support the broad premise that chromates should be kept out of or maintained at the lowest possible level in drinking water until completely contrary data are available. At least, the United States Public Health Service in its latest drinking water standards retained 0.05 mg/l as a mandatory maximum limit for water used by interstate carriers.

Is there any chance that the toxic form of chromium is not the chromate itself but the trivalent chromic ion formed in the living tissue? Observations of the chromic ion in solution under similar test situations with bacteria show some toxicity for the chromic state. No chromosome aberrations are produced in the cells of higher animals while the extent of the depression of respiration rate and the number of growing bacterial organisms are similar. The authors believe that the chromic ion is not responsible for the chromate toxicity observations.

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TECHNICAL SESSIONS



"PLANNING A COOLING WATER TREATMENT
PROGRAM FOR WASTE AND POLLUTION CONTROL"

by

T. F. DALTON

Historically, the basic consideration given to cooling water treatment was that of an economic one. Was it more expensive to prevent corrosion and scaling or to invest in the maintenance and repair of these systems after the scale and rust have accumulated? Many people found it more advantageous to periodically clean and manually rehabilitate the system rather than use even the basic types of chemical treatments.

As the flow rates and velocities increased and a greater demand for cooling manifested itself, operating engineers gradually found that periodic dosages of chlorine to arrest the growths of slime and algae helped to keep their equipment from fouling quite as fast and prolonged the operating life of the equipment. Allowing quantities of water to overflow also prevented scaling and fouling. This method was expensive due to the quantities of water involved, especially if the source of the cooling water was a municipal system. As the pumping rates increased, maintenance costs and water costs steadily climbed, forcing many companies to look to other sources of water and the use of recirculating systems. In addition, as the more sophisticated types of chemical treatment came into being, operating personnel found that cleaning could be regulated on a routine basis, and all prior unscheduled outages or downtime were virtually eliminated.

CONSERVATION AND POLLUTION

With the advent of water conservation programs and pollution control, water re-use has become a more critical problem. The demand for a constant supply of quality water which can be treated for industrial uses and potable use, forces many engineers to review their cooling water treatment programs to see if they can chemically treat the systems properly and economically, while, at the same time, not add to the industrial waste problem.

Today, it is not only possible to have a cooling water treatment that will be technically feasible and economical, but one which will fall within the parameters of pollution, set up by local and state health agencies. When we say technically feasible, we mean if the chemical treatment prevents scaling and retards corrosion and does not add to the waste disposal problem. It will be economical if it reduces labor costs, prevents lost production and eliminates unscheduled shutdowns.

A cooling water treatment program should also meet with local, state and federal regulations regarding wastes treatment and pollution abatement. The late President Kennedy had this to say about our water pollution problem: ".....we must establish as a principle of law and good sense that no one any longer has the right to pollute. We must insist that everyone who withdraws water from whatever source must be prepared to give that water back again as clean as modern technology knows how to make it."

To have effective pollution control, the local-state-federal governments all must be willing to contribute and all must respect each other's position in solving the problems. The concept of pollution control involves research, money, engineering, construction, education, co-ordination and policy. Government, industry and schools can each find a segment to work on. By sharing information, by providing research, and by appropriate legislation, pollution can be mitigated.

The purpose of this paper is to examine several cooling water treatment problems and the chemical treatments recommended to solve these problems to see which of

these will be technically and economically feasible, also taking into consideration waste treatment and pollution control.

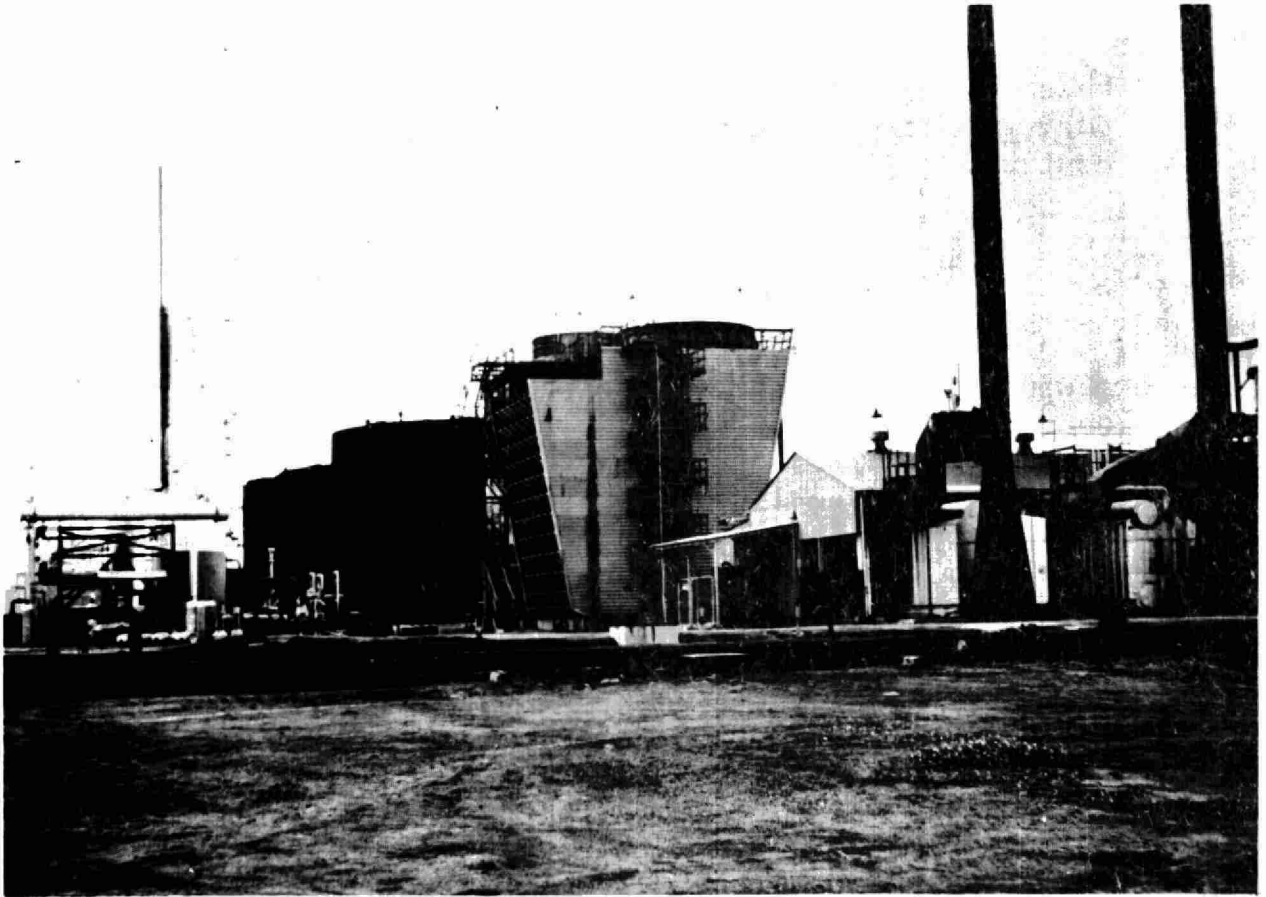
COOLING TOWER OPERATION

The function of cooling water is to provide a medium for the exchanging of heat whether the system be open or closed.

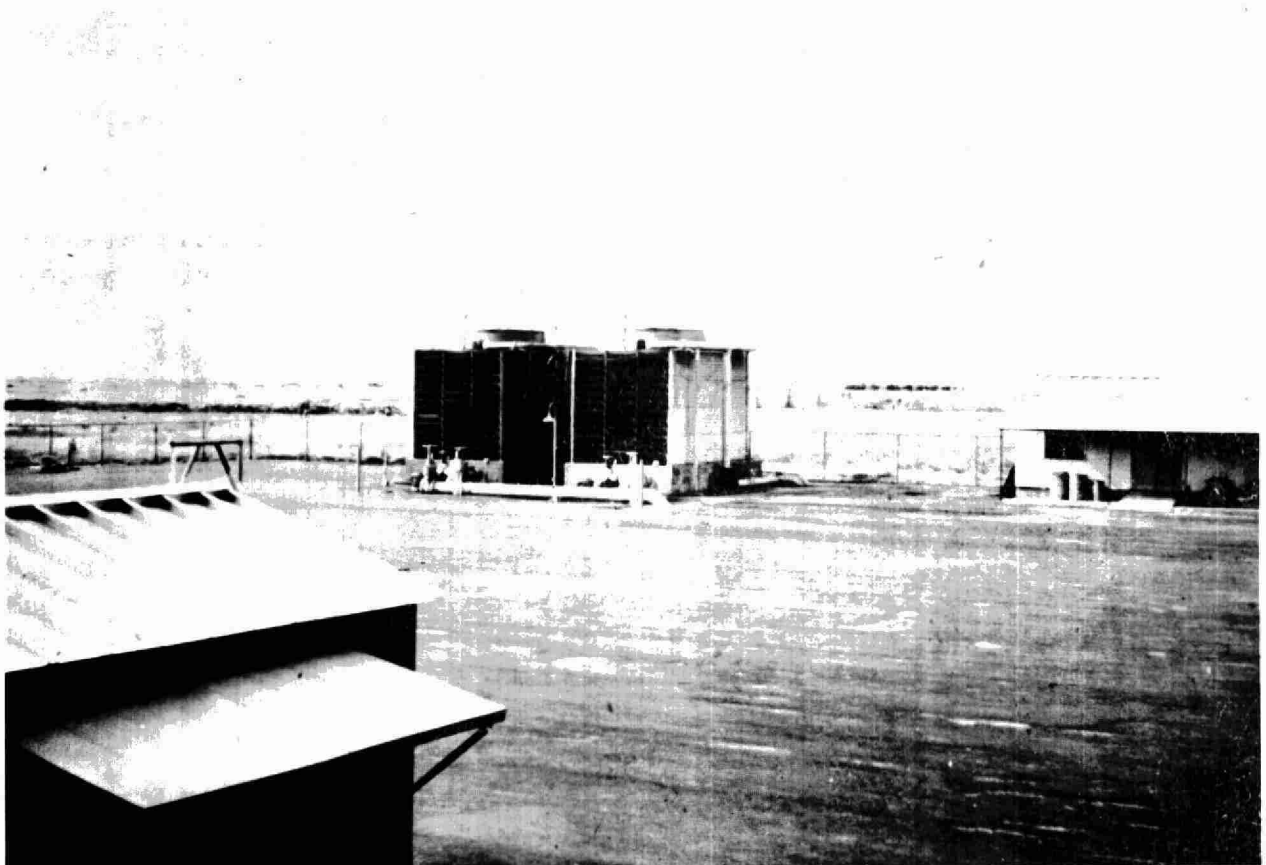
The cooling tower, with which all of you are familiar, receives the heated water after it has picked up heat from equipment which has been cooled. As the water enters the top of the tower, it spills onto a tray, drains through small orifices and falls to the pan of the tower located on the bottom. Along the way, the water is broken up into small particles by the baffles in the tower and is intimately mixed with air. The air comes through the side louvres, aided by an induced fan located on top of the tower causing the air to pass through the minute drops of water on a counter-flow principle.

The air evaporates a quantity of water, depending on the relative humidity and temperature. As the water evaporates, it takes up the heat, cooling the portion that is left behind to fall into the pan. The evaporation of one-pound of water from a cooling tower accounts for a heat loss of 1,000 BTU. This is equivalent to cooling 100 pounds of the water remaining in the pan by 10°F. Actually, the water in the pan is generally 8°F - 12°F cooler than the inlet water at the top. A circulating pump then recirculates this cool water through the system again to transfer heat from the equipment.

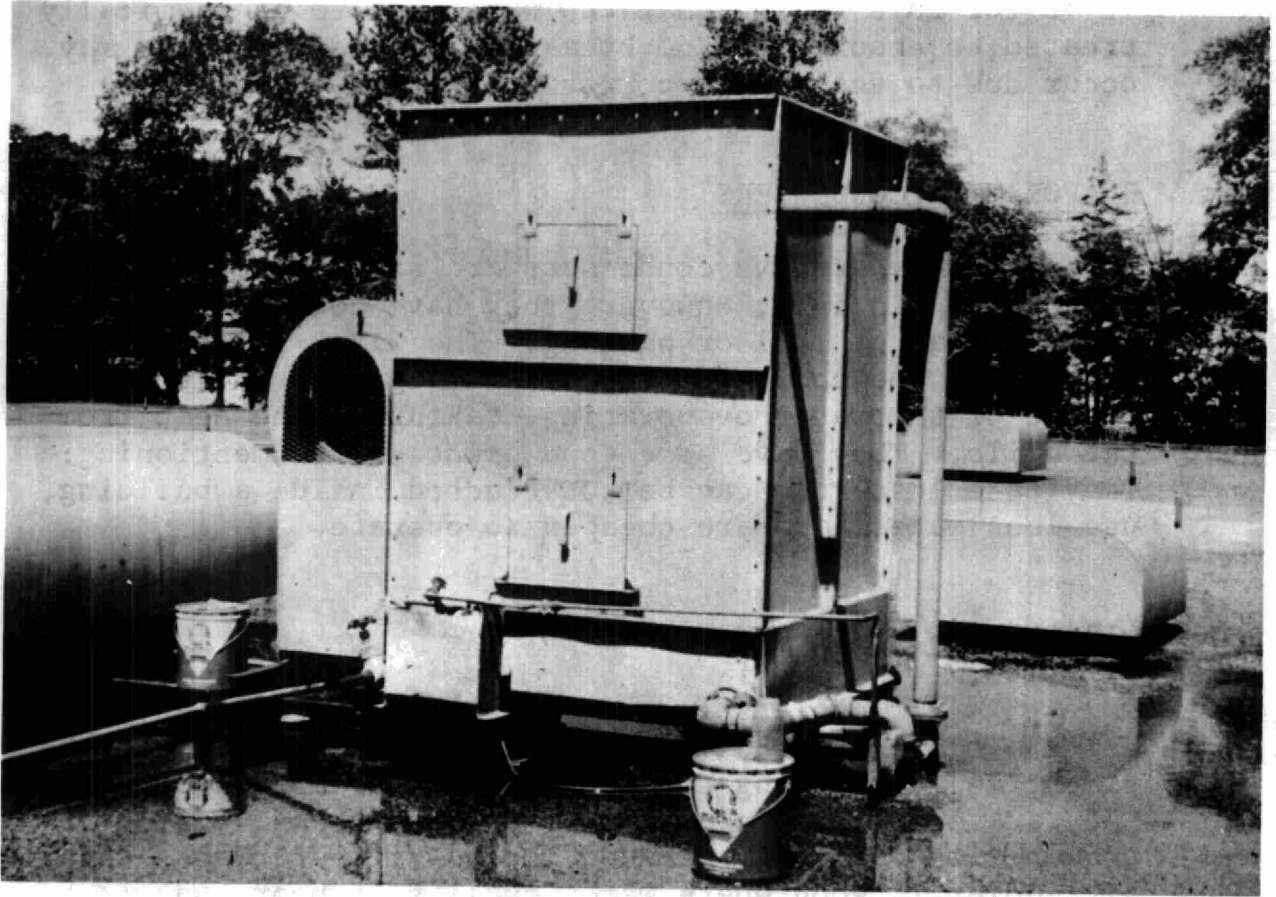
The equipment to be cooled consists of the compressor, which becomes hot during the compressing of the refrigerant from a gas to liquid, and the condenser which is a type of tube and shell heat exchanger that functions to cool the hot compressed liquid refrigerant. From the condenser, the cooled refrigerant goes to the receiver tank or reservoir, then through an expansion valve at the evaporator where it undergoes a change of state. The expansion changes the liquid into a gas reducing the



Cooling Tower in Petrochemical Plant



Counterflow Cooling Tower



INDUSTRIAL COOLING TOWER

temperature of the refrigerant giving a cooling effect thus completing the heat exchange cycle.

The cooling water functions to act as an intermittent heat exchanger and coolant, and also undergoes several chemical changes in going through the heat exchange cycle. It is for this reason that the water has to be chemically treated to ensure that no breakdown of the equipment may occur due to scaling or corrosion in the system.

EVAPORATIVE CONDENSERS

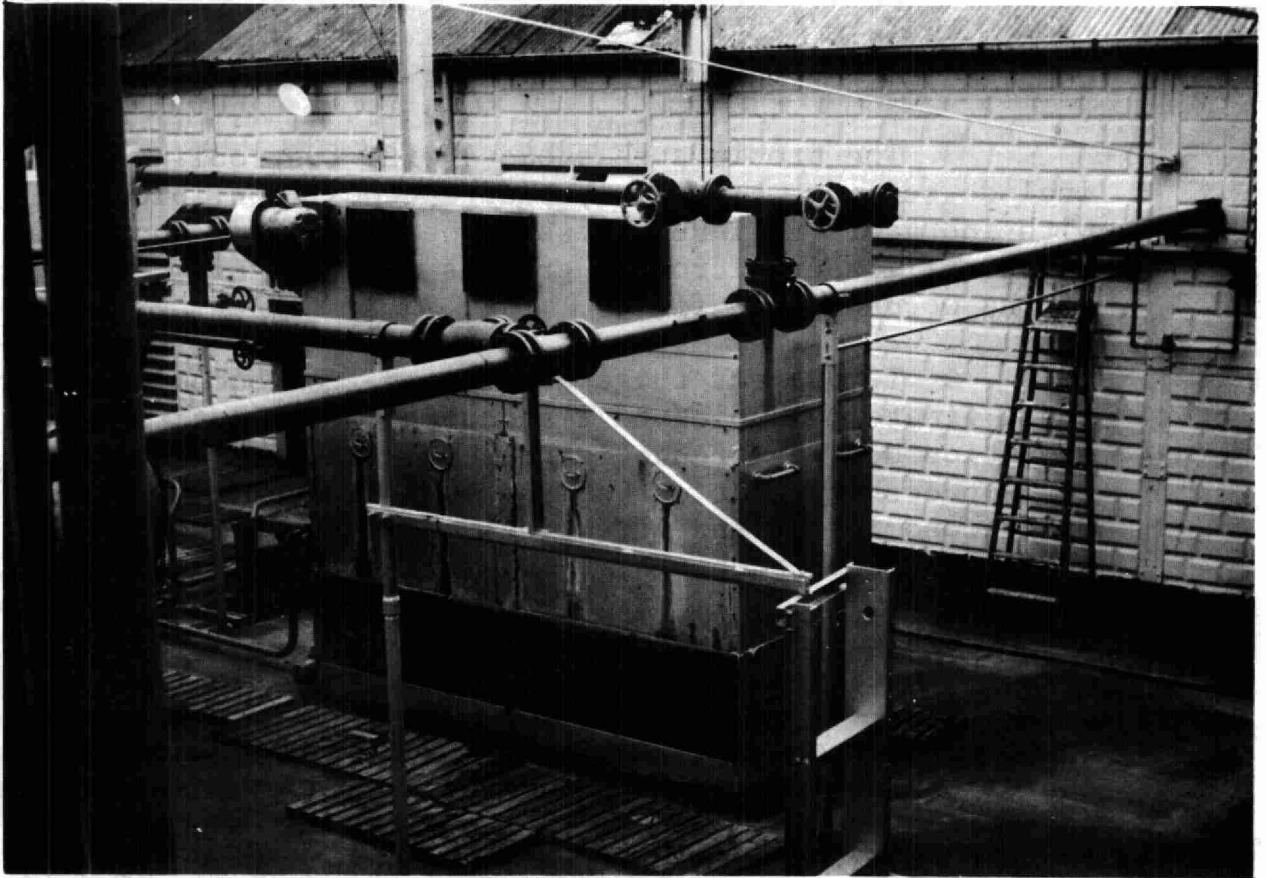
Evaporative condensers are similar to cooling towers in principle; however, they have coils inside of them instead of fill or packing. The water falls in drops over the coils cooling the refrigerant due to a small amount of the water evaporating, taking up the heat from the coils. They have some good points worth mentioning: They take less room can be constructed inside a building, use less water, and are cheaper to operate.

AIR COOLERS

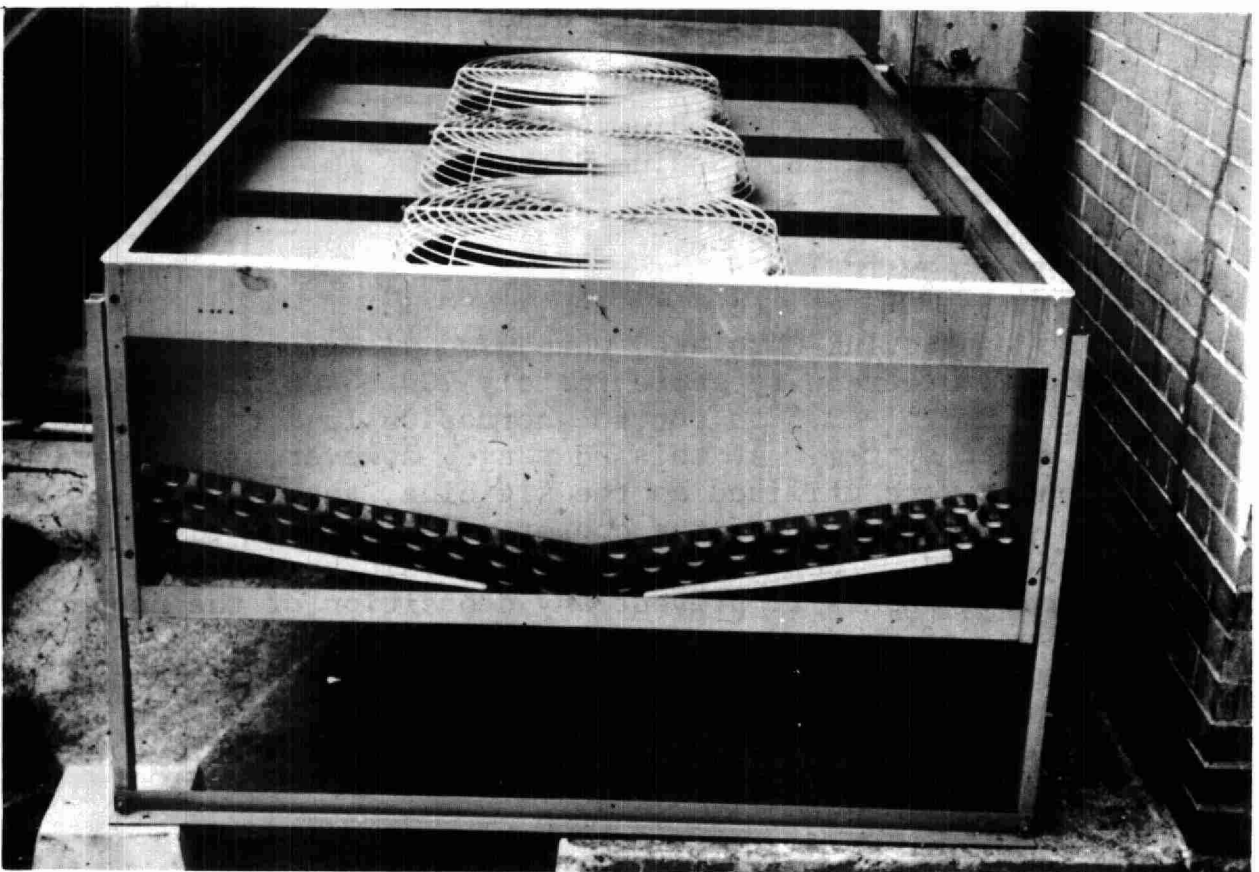
Air coolers function, as the name implies, to bring air over the coils to effect a cooling while at the same time eliminating the need for large amounts of water. They are excellent in a small system by themselves or in conjunction with a larger cooling tower operation. The air cooler is good where water quality is poor and quantity is scarce.

We will not go into detail on problems relating to air coolers or evaporative condensers at this time.

The same is true for cooling ponds, stabilization lagoons and spray ponds. In contrasting area or size, however, it is interesting to note that a cooling pond must have about 20 times the area of a spray pond, and from 500 to 1000 times the area of a cooling tower to effectively perform its function.



Evaporative Condenser



Air Cooler

COOLING TOWER PROBLEMS

The problems that occur with the cooling water include scaling, corrosion, sludge deposition, plugging with inorganic residues, loss of heat transfer due to organic films or microbial growths and delignification of the wooden tower fill.

To prevent these conditions from becoming severe and ultimately leading to a shutdown of the entire operation due to a reduction of heat transfer efficiency, it is necessary that we examine several chemicals which will economically and effectively prevent or reduce the above-mentioned problems. However, in terms of technical feasibility, it is important to consider the waste control and possible pollution problem which may result if the chemical treatment recommended is not suitable.

For example, let us consider two types of corrosion inhibitors that have been found to be effective in treating cooling waters. If we consider these inhibitors and contrast their effectiveness in a given system, we can see that, in terms of pollution control and effective corrosion control, our choice is narrowed considerably when we examine other factors. The two corrosion inhibitors are:

- A. Sodium Chromate
- B. Sodium Nitrate

SODIUM CHROMATE

Sodium Chromate, when used alone in an alkaline media, would require approximately 200 - 400 ppm in a pH range of 7.5 - 9.5 to control corrosion in a typical cooling tower system. At this pH range, however, if copper sulphate were utilized as the algicide, there would be some precipitation of the copper as either the carbonate or hydroxide. Our initial thought would be to change algicidal agents to prevent any deposition of the copper. However, if we were to couple a polyphosphate with the chromate, as little as 20 ppm of the chromate would be required to inhibit the corrosion. The pH range can be dropped to 6.5 - 7.5, thus reducing the possibility of

copper deposition. Using a combination of chromate - polyphosphate would be helpful in other ways by:

- A. Reducing the chromate concentration contained in the bleed-off or blowdown water.
- B. Reducing alkalinities, thus minimizing the precipitation of calcium phosphate.
- C. Reducing total dissolved solids in the system.
- D. Making it possible for complete removal of the chromate ion by the new ion exchange resin system, which has just recently been developed.

This new system, when fully perfected, may not only allow for removal of the chromate from the bleed-off or waste water, but will ultimately aid in the recovery of these chemicals for re-use. Therefore, in terms of technical feasibility, economics and pollution control, this method could provide the means to achieve all desired end results.

SODIUM NITRATE

The use of sodium nitrate as an inhibitor in cooling water and recirculating systems has long been utilized, especially in areas where the proximity of water intake systems to waste discharge systems is very close. In terms of river pollution, sodium nitrate when used in concentration of 300 - 500 ppm, in a pH range of 7.0 - 9.0, has worked satisfactorily to control the corrosion and, more important, has actually aided in some waste treatment programs by providing nitrates for the biochemical systems living in the river. The addition of nitrogen, as well as other inorganic compounds, such as phosphorous, are essential to the metabolic growth of micro-organisms.

Specifically, the addition of nitrates to the waste water provides a source of oxygen for the aerobic

bacteria which stabilizes the wastes. Since organic wastes have a high BOD (biochemical oxygen demand), their presence in any mixed effluent of waste water may exhaust the oxygen normally present. This results in the decline of aerobic bacteria and the development of anaerobic bacteria, causing the decomposition of the wastes to proceed with the formation of gas and malodors.

The addition of an enriched solution of nitrates from a cooling tower effluent helps to reduce the BOD indirectly by encouraging the growth of algae and aquatic flora which produce additional oxygen for the stream through photosynthesis.

W P C RATING

Table I lists a group of chemicals which are normally used to treat cooling water systems. For purposes of classification, they have been grouped according to their basic functions, such as algicides, pH adjustment, scale control, corrosion control and dispersing agents.

In each group of products, there are two ratings which will help to pick out that product which best meets the need of a treatment which is technically feasible and economical. There is also a consideration given for the overall evaluation of the chemical, in terms of a water pollution control rating (WPC rating). The water pollution control rating measures the overall effectiveness of the product from the standpoint of toxicity, efficiency of performance, and in terms of the treatment required to remove the product from the waste effluent before it is introduced into a stream or river. The lowest rating on the WPC scale is 1 with the highest being 5.

Since there are many variables to consider in terms of dosage concentration, effectiveness as inhibitors, and compatibility with other treatments, there may be other considerations or criteria to evaluate these various types of chemicals. The WPC rating and cost factor represent only two such criteria which may help to distinguish between the various chemicals. Ratings can be worked out for all types of chemicals, incorporating many other standards.

TABLE I

TABLE OF COOLING WATER CHEMICAL TREATMENTS

<u>Name</u>	<u>Purpose</u>	<u>Usual Dosage</u>	<u>Receommended Testing Procedure</u>	<u>WPC Rat- ing</u>	<u>Waste Problem</u>	<u>Remova</u>	<u>Cost Factor</u>
1. Chlorine	Algicide	2-10 ppm	Colorimetric, orthotolidine	2	None	None	1
2. Quaternary Ammonium Chloride	Algicide	10-30 ppm	Colorimetric, QAC test	1	None	None	4
3. Copper Sulphate	Algicide	0.1-1.0 ppm	Spectro-photometer	4	Precipitation with high alkalinities toxic to fish	Coagulation, filtration	2
4. Sodium Pentachlorophenate	Algicide	2-5 ppm	Spectro-photometer, Aminoantipyrine	5	Highly toxic to aquatic life also taste & odor agent in potable water	Bio-oxidation, trickling filter	3
5. Sulphuric Acid	Adjust pH	Continuous as required	Electrometric pH or titration	2	Acidic wastes can be corrosive; also toxic to aquatic life	Neutralization with alkaline waste or lime	1

	<u>Name</u>	<u>Purpose</u>	<u>Usual Dosage</u>	<u>Recommended Testing Procedure</u>	<u>WPC Rating</u>	<u>Waste Problem</u>	<u>Removal</u>	<u>Cost Factor</u>
6.	Sulphamic Acid	Adjust pH	Continuous as required	Electrometric pH or titration	2	Acidic waste toxic to aquatic life	Neutralization with alkaline waste or lime	2
7.	Citric Acid	Adjust pH	Continuous as required	Electrometric pH	2	Acidic Waste	Neutralize with alkaline waste	3
8.	Sodium Tripolyphosphate	Scale-Corrosion Control	5-40 ppm	Colorimetric, phosphomolybdic ion	1	None	None	2
9.	Sodium ethylene diamine tetraacetate	Scale Control	2-20 ppm	Titration with CaO ₂	1	None	None	3
10.	Disodium phosphate	Scale Control	10-30 ppm	Colorimetric blue phosphomolybdic ion	2	Will precipitate out in highly alkaline water	Sedimentation	1
11.	Sodium chromate	Corrosion Control	20-200 ppm	Colorimetric, spectrophotometer	5	Highly toxic to aquatic life. Will affect water potability.	Ion-exchange resin	3

	<u>Name</u>	<u>Purpose</u>	<u>Usual Dosage</u>	<u>Recommended Testing Procedure</u>	<u>WPC Rat- ing</u>	<u>Waste Problem</u>	<u>Rem val</u>	<u>Cost Factor</u>
12.	Sodium nitrate	Corrosion Control	100-500 ppm	Colorimetric, brucine test	3	Can affect water potability	Bio oxidation tri kling fil er	2
13.	Sodium Silicate	Corrosion Control	10-40 ppm	Colorimetric	1	May cause Precipitation	Non	1
14.	Nonionic Surfactant	Dispersing Agent	0.5-3.0 ppm	Colorimetric	2	Can Cause Foaming, Interferes with Coagulation	Fil ration	2
15	Sodium Ligna-sulphonate	Dispersing Agent	2-20 ppm	Viscosimeter	1	Can Interfere with Coagulation	Fil ration	1

ALGICIDES

In terms of algicides, for example, the quaternary ammonium chlorides present the least problem from the standpoint of a pollution control or waste removal situation. However, in terms of cost, they are the highest in cost of the four products considered for use as algicides. Copper sulphate and sodium pentachlorophenate, in addition to having a high water pollution control rating, rank second and third in cost and have removal problems, hence the choice of a satisfactory algicide rests between chlorine and the quaternary ammonium chloride compounds. Since chlorine has a low WPC rating and is the lowest in terms of cost, it therefore becomes the best product in terms of technical feasibility and economy to use as an algicide in cooling tower systems. This does not rule out the use of products such as chromated-copper arsenate for use as a wood protection against fungi. In many cases the use of the exotic or highly toxic materials for a specific problem is justified and can be controlled by special procedures.

In cooling towers where chlorine is used as the algicide and the tower fill consists of redwood, care must be taken to ensure that the pH does not exceed 7.5 and that the chlorine content remains below 1 ppm. The control of the pH to prevent delignification of the redwood is not as critical where non-oxidizing types of algicides are used. The chlorine dose should also be made on an intermittent basis to minimize attack on the redwood.

INHIBITORS

In a comparison of inhibitors, such as the sodium chromate and sodium nitrate which was contrasted before, the chromate has a WPC rating of 5 and a cost factor of 2, whereas the sodium nitrate has a WPC rating of 3 with a cost factor of 1. Hence, the logical choice would be nitrate. However, today, the use of chromates for tower treatment is far more prevalent because of their effectiveness as an inhibitor plus the fact that chromates are beneficial to treating redwood.

SCALE PREVENTION

When we come to the scale prevention compounds, the choice narrows down to polyphosphates and EDTA (ethylene-diaminetetraacetic sodium salts). In terms of cost factors and WPC rating, the polyphosphates still are preferred. In actual operation, however, there are still such things as phosphate sludges or phosphate bloom to contend with, which are associated with polyphosphates alone. In most cases, the polyphosphates are used in conjunction with other chemicals - chromates, sodium ferro-cyanide, zinc sulphate, sodium lignosulphonate, and surfactants. The combination of these other materials adds or reinforces the effectiveness of the polyphosphates but creates an entirely different waste disposal program.

Polyphosphates function as better inhibitors and scale preventers than orthophosphates at lower pH ranges (7.0 - 8.0) and at higher concentrations (30 - 50 ppm). The addition of some metal cation such as zinc sulphate functions as a synergist with the polyphosphate to give the desired result and to increase the rate of reaction.

The EDTA salts can best be utilized as an alternate treatment for scale control much in the same fashion as one changes algicides. EDTA products will not only sequester hardness, but also initiate a self-cleaning of the system to remove the residual amounts of calcium phosphate.

ADJUSTING pH

For adjusting pH, the cost of sulphuric acid and its effectiveness clearly indicate its choice for this type of product. The problem of pH adjustment can be complicated by many factors. Generally, well waters or waters high in CO₂ lose the carbon dioxide as a gas from the cooling tower causing the alkalinity to rise. As the alkalinities rise, the solubility of the calcium carbonate decreases, causing the formation of scale. The addition of sulphuric acid will prevent the decrease in calcium salt solubility. Other factors, such as high iron content, high silica, or the presence of silt, clay, or alumina from surface water can induce this precipitation. These other chemical factors can be accounted for by modification of the treatment and bleed-off from the tower.

BLEED-OFF

There are many situations encountered in treating a cooling tower that can only be solved by a properly controlled bleed-off. Bleed-off rates can be regulated and controlled by automatic equipment. This is true of all phases of the cooling water treatment program where continuous analyzers, recording pH meters and conductivity cells all play an important role.

By the use of a pre-calibrated and pre-set conductivity meter connected to the blowdown valve with a cycle timer, a cooling tower can be properly bled-off. Normally, the cycles of concentration are formulated or based on the hardness of the make-up water entering the system. The chart below serves as a rough guide:

<u>Hardness in Grains per Gallon</u>	<u>Cycles of Concentration</u>
2.0 (under) gpg	6
2.1-3.5 gpg	5
3.6-7.0 gpg	4
7.1-10.5 gpg	3
10.6 (over) gpg	2

DISPERSING AGENTS

Sodium lignosulphonate, by virtue of its cost and excellent dispersing powers, can be used to treat cooling tower waters to prevent the formation of sludge and scale. The use of surface active agents such as the nonionic types of ethylene and polypropylene oxide alkyl phenols function as dispersing agents and anticrystal agents in scale prevention. The cost of these surfactants has come down in the past years allowing them to compete on a cost basis with the alginates, carboxymethyl cellulose lignosulphonates and polyelectrolytes which are used as dispersing agents in cooling water systems.

There is one drawback with surfactants as dispersing agents, namely the problem of detergent pollution which interferes not only with normal coagulation and filtration, but also causes unsightly foaming in rivers and plant outfalls.

With the advent of biodegradable detergents which are coming out more and more each day, there may be an increase in the use of surfactants, especially the low-foaming variety, for treating recirculating water systems. These biodegradable detergents may serve as a new source of oxygen to meet the need of the high BOD effluents

COOLING TOWER CLEANING

The treatment discussed so far can only be considered an insurance that operations will not break down. Real care of cooling tower systems calls for the periodic cleaning of towers to physically and chemically remove undesirable soils. There are generally two types of cleaning which would be of benefit to cooling towers. They are:

- A. Alkaline cleaning to remove oils, slime, algae, silt and sludge. This type can be done at any time, but it is recommended in the spring before the tower is put on the line.
- B. Acidic cleaning to remove scale, corrosion deposits and sludge. This type of cleaning can be done at any time during the season; however, it is recommended to be done at the end of the season.

The cleaning of towers can pay off in terms of heat-transfer efficiency, especially in a year-round cooling situation. Radical changes in pH which are normally experienced in a tower cleaning, together with the surfactants present in such cleaning compounds, tend to loosen the network of algae roots and scale crystals that fill the interstices of the tower. Chemical treating the towers will conserve and protect them but chemical cleaning will maintain their efficiency.

TABLE II

INDUSTRIAL RATING FOR WATER CONSUMPTION

<u>Industry Name</u>	<u>Gallons Water Per Unit</u>	<u>Unit Designation</u>	<u>Rating (Total Units Produced)</u>
Steel	65,000	tons	1
Petrochemical	1,100	bbls	2
Paper	39,000	tons	3
Paperboard	15,000	tons	4
Coke	3,600	tons	5
Cane Sugar	1,000	tons	6
Beer	470	bbls	7
Whiskey	80	gals	8
Canning	75	cases	9
Textiles	70	lbs	10

ALTERNATE USES OF COOLING WATER

There have been several suggestions made with respect to pollution control, water conservation, and proper methods to operate a cooling tower system.

A power generation station in Indiana uses the 7 million gallon per day effluent from the local sewage treatment plant as the main source of condenser cooling water. The sewage effluent containing the detergents, phosphates and proteins receives a minimum of chemical treatment prior to entering the cooling system consisting of sulphuric acid for pH control and chlorine for slime and algae control. There are no problems with ammonia from the sewage as was previously expected. Instead of copper corrosion the ammonia is apparently stabilized biologically or lost through aeration. This re-use of the sewage effluent conserves other water sources and does a satisfactory job.

Hynes, in his book, "The Biology of Polluted Waters", states another extreme use of cooling water effluent to minimize the problem of thermal pollution.

He would copy the farmers in Iceland who use hot water geysers to heat the glass green-houses to grow plants. Hynes states, "It would seem that a few acres of green-houses would be a more profitable and sensible adjunct to a factory or power station than a number of cooling towers." This, of course, may be far fetched in terms of modern day farming; however, it is the thought that should be considered. There should be other uses made of cooling water and power plant effluents. A possible suggestion would be to utilize the millions of BTU's in the cooling water for some type of heating purpose, such as a hot water recirculating system under roadways to prevent ice formation, or perhaps, for the sports enthusiast, hot water heating of stadium seats by means of a cooling water effluent from a nearby power plant.

Cooling towers themselves have been put to other uses, such as the waste water treatment application in a paper mill reported by Finnerty. This paper mill employed a modified activated sludge process similar to that found in a municipal sewage plant. Based on a previous experience it was found that the optimum temperature for operation was 92°F. When the temperature went above this point, biological activity decreased. At 100°F, the biological activity was reduced by 40 - 50 per cent. Over 100°F there was a danger that the activated sludge system would be destroyed, if not greatly upset.

To prevent the reduction of biological activity an induced-fan counterflow cooling tower was put into the system before the activated sludge tank. By means of a thermostat and variable pitch fan, the tower is now able to maintain the temperature at or around 92°F. When the temperature is below 92°F, the water bypasses the tower.

The cooling tower does more than cool the liquid here. It also oxygenates the systems, cutting down on BOD and chlorine demand. It also eliminates the problem of thermal pollution in the receiving stream aiding in the reoxygenation and stabilization of the river.

CONCLUSION

There is no one plan or treatment that will solve all of the problems of treating cooling towers with chemicals while trying to prevent pollution. There are instances where external or pretreatment, such as filtration and softening, may be helpful, but for large quantities of water it is uneconomical.

Inasmuch as waste treatment and pollution control involve knowledge of microbiology and biochemistry, whereas cooling water treatment involves mainly chemistry, it is essential that engineers acquire some knowledge of these other subjects. Biological systems are dynamic, hence the design of these systems must reflect this type of thought.

What is needed is a look at what criteria will be used to judge the effluent? How will your effluent affect the stream and your neighbor down stream? Once you have these facts in mind, work back to the plant and design your system to give this effluent.

The cooling water system and the cooling tower can form an integral part of your waste treatment and water conservation program. Fundamental knowledge of the biological phenomena and chemical forces will aid you in putting the tower and the water to best use. Pollution control, waste treatment and water conservation all call for challenging thoughts and ingenuity, both in design as well as execution.

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THE BANQUET



"THE ST. CLAIR RIVER RESEARCH COMMITTEE -
A CO-OPERATIVE APPROACH TO POLLUTION
ABATEMENT

by

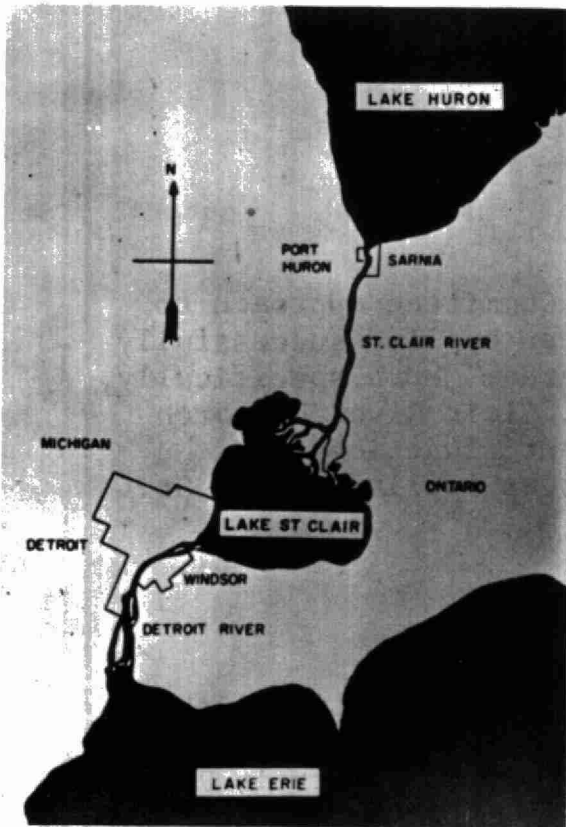
C. M. FINIGAN

INTRODUCTION

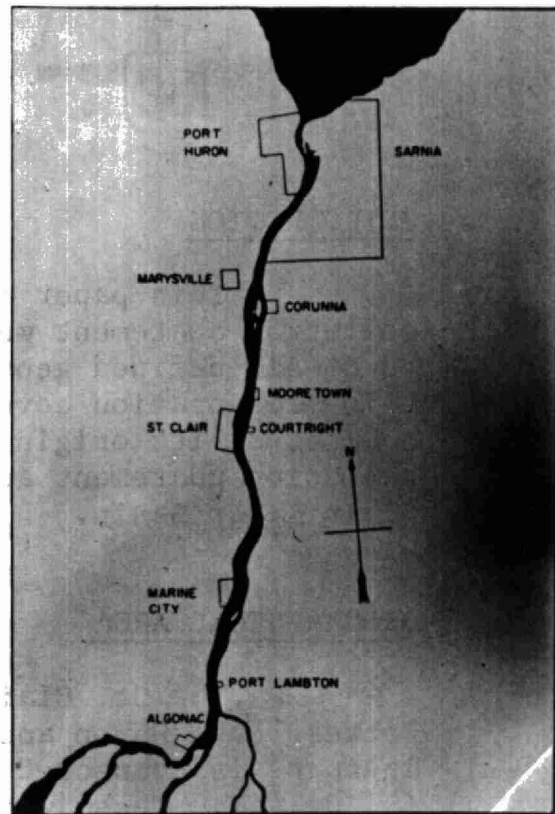
This paper outlines a Committee approach to pollution abatement which has been applied successfully to a well-defined geographical area. More specifically, this presentation covers the St. Clair River Research Committee, its origin, development, functions and pollution abatement achievements as applied to the St. Clair River Basin.

GEOGRAPHICAL AREA

The St. Clair River is the connecting link between Lake Huron and Lake St. Clair, a small lake which, in turn, is connected to Lake Erie by the Detroit River (Slide #1). These water bodies form the International Boundary between the Province of Ontario and the State of Michigan. The St. Clair River is approximately 40 miles long, beginning at Lake Huron and flowing in a south-westerly direction to its mouth at Lake St. Clair. The upper river is characterized by a rather uniform width of one half mile with some broadening occurring at Stag Island and at Woodtick Island. The lower river, beginning at Walpole Island, broadens out and is characterized by many islands and shallow expanses (Slide #2).



Slide #1



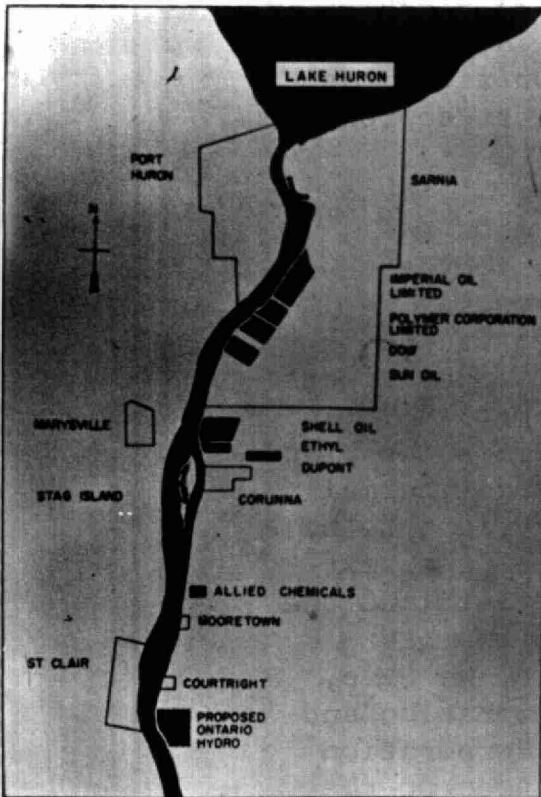
Slide #2 and #18

Population is concentrated at the head of the river in the cities of Port Huron, Michigan (36,000) and Sarnia, Ontario (50,000). A number of smaller communities are distributed down river, as shown, with total population on both sides approximating 107,000.

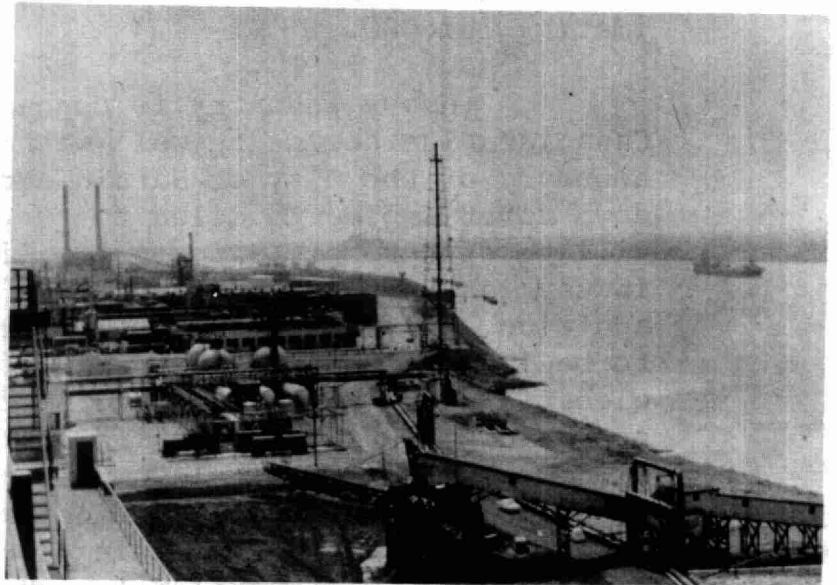
Heavy industry is concentrated on the Canadian side beginning well within the southern boundary of the City of Sarnia and stretching down river another 8 miles to just south of the Village of Corunna (Slide #3). Eight of the largest industries in this area are based on petroleum. In addition, the Ontario Hydro Electric Commission plans to begin construction next year of a large thermal electric power plant just south of Courtright to be operational in 1969. Looking down river, the next slide shows Dow Chemical Company on the left and the power plant at Marysville, Michigan, in the background (Slide #5). Proceeding southward, we have, in order, Sun Oil, Shell Oil, Ethyl Corporation and DuPont. The next slide pictures Ethyl Corporation in the foreground, with Shell Oil of Canada to the right (Slide #6). These, then illustrate the industrial complex that has evolved to date along the Canadian side of the St. Clair River.

COMMITTEE ORIGIN

Since it is an international boundary, pollution control of the St. Clair River is under the jurisdiction of the International Joint Commission. The first extensive pollution survey in this area, carried out by this Commission in 1944-46, indicated that, although the St. Clair River had not reached a critical stage of pollution, future expansion in the Sarnia industrial area could create a serious situation. The late Dr. R. K. Stratford, then president of the Ontario Research Council, recognized



Slide #3



Slide #5



Slide #6

MAIN FUNCTIONS OF THE
ST. CLAIR RIVER RESEARCH COMMITTEE

1. TO STUDY AIR AND WATER POLLUTION IN THE ST. -
CLAIR RIVER BASIN, SPECIFICALLY TO MEASURE
CONTAMINANT LEVELS AND TO ESTABLISH SOURCE
LOCATIONS.
2. BASED ON THESE STUDIES TO RECOMMEND TO
APPROPRIATE MANAGEMENT CORRECTIVE ACTION WHERE
WARRANTED.
3. TO ASSESS THE EFFECTIVENESS OF ANY REMEDIAL
ACTION.
4. TO PUBLICIZE COMMITTEE ACTIVITIES AND THEREBY
MAINTAIN GOOD PUBLIC RELATIONS.

Slide #7

this possibility and proposed, as a preventative measure, the formation of a permanent pollution study group, composed of representatives from local industry and the Ontario Government. On February 22, 1952, Professor A. C. Plewes and Dr. R. K. Stratford, of the Ontario Research Council, interviewed officials from Imperial Oil Limited, Polymer Corporation and Dow Chemical of Canada and found them favourable to the formation of such a group. The St. Clair River Research Committee was subsequently formed on March 8, 1952 and was charged with the responsibility of applying a co-operative approach to the prevention and solution of industrial pollution problems in the Sarnia area.

FUNCTIONS

Since its inception the Committee has functioned solely as a fact-finding and not as a regulatory body. Its main functions are briefly as follows (Slide #7):

1. To study air and water pollution in the St. Clair River basin, specifically to measure contaminant levels and to establish source locations.
2. Based on these studies to recommend to company management corrective action where warranted.
3. To assess the effectiveness of any remedial action.
4. To publicize all committee activities and thereby maintain good public relations for the benefit of the participating industries.

The Committee engages the Ontario Research Foundation to perform measurements, correlate data, and conduct special studies on air pollution. Similar services in the water pollution field have been provided by a consulting biologist, the industries themselves, and the Ontario Water Resources Commission.

The Committee is currently operating on an annual budget of \$40,000 borne wholly by the participating industries and apportioned according to the number of employees and total assessment. The Provincial Government contributed \$9,000 annually to the end of 1963 but this grant has now been withdrawn.

MEMBERSHIP AND OPERATION

The following eleven industries and the Ontario Department of Health each have one voting member on the present Committee (Slide #8):

Cabot Carbon of Canada Ltd.
Dow Chemical of Canada Ltd.
DuPont of Canada Ltd.
Ethyl Corporation of Canada Ltd.
Fiberglas Canada Ltd.
Holmes Foundry Ltd.
Imperial Oil Enterprises Ltd.
Mueller Ltd.
Polymer Corporation Ltd.
Shell Canada Ltd.
Sun Oil Company Ltd.

Membership is strictly voluntary and invitations are extended to all new industries entering the area.

The Committee meets monthly to discuss the results of the area surveys and other matters of mutual interest. Company management is invited to at least one of these meetings where questions are received on the operating budget, the study program, major pollution problems, etc. A press release is usually prepared to cover the proceedings of these Management meetings.

ACHIEVEMENTS

It could be reiterated that the Committee, as such, assesses and recommends only! Tangible action is the sole responsibility of individual company management. The quantity and cost of pollution abatement facilities installed without compulsion by the various membership

companies is, therefore, a direct measure of the effectiveness of the Committee. Capital expenditures on water pollution abatement in this area since 1955 have been as follows: (Slide #9).

<u>Year</u>	<u>Expenditure</u>
1956	\$ 842,000
1957	704,000
1958	733,000
1959	974,000
1960	715,000
1961	339,000
1962	356,000
1963 (estimated)	340,000
<hr/>	
Total	\$5,003,000

With the co-operation of my colleagues on the committee, and the very kind permission of their managements, I have been able to obtain some coloured photographs of recent abatement equipment installed by some of the companies situated along the river. I would comment on these as follows:

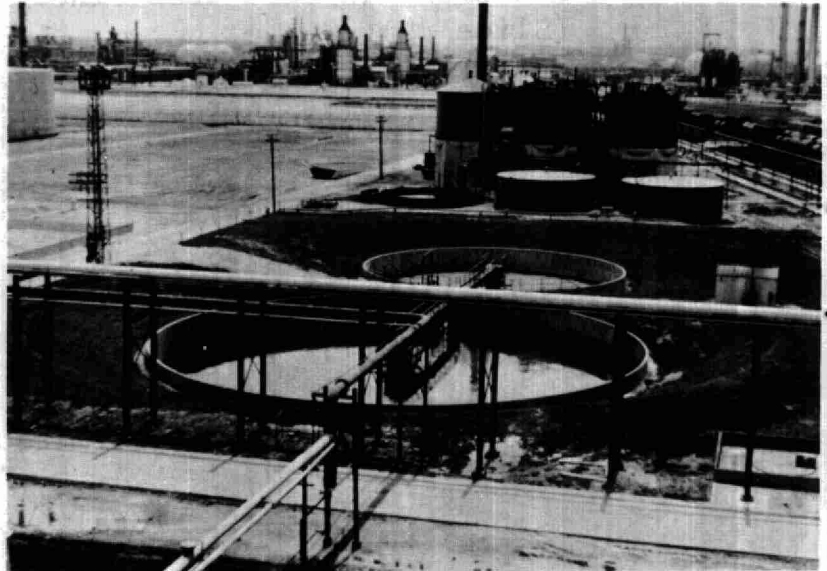
1. Imperial Oil Enterprises Ltd. -

One of the major waste problems encountered by any refinery is that of phenol disposal. Imperial Oil have chosen deep-well disposal for these materials, with five such wells constructed to date at a cost of approximately \$275,000. Details of these installations are contained in a paper presented at the 1961 session of this conference by Mr. I. C. MacLeod. Not being able to get a picture of an underground disposal well, I have, instead, one of typical equipment installed at Imperial to minimize oil discharges to the river. The next slide (Slide #10) shows oil sludge removal facilities (settling and centrifuging) in the background with two circular oil separators in the foreground. The next slide (Slide #11) provides a closer view of the oil separators showing the rotating

MEMBERS OF ST. CLAIR
RIVER RESEARCH COMMITTEE

<u>COMPANY</u>	<u>OPERATING BUDGET ASSESSMENT</u>
CABOT CARBON OF CANADA LTD.	2.0
DOW CHEMICAL OF CANADA LTD.	12.0
DUPONT OF CANADA LTD.	2.2
ETHYL CORPORATION OF CANADA LTD.	2.0
FIBERGLAS CANADA LTD.	2.9
HOLMES FOUNDRY LTD.	3.0
IMPERIAL OIL ENTERPRISES LTD.	30.9
MUELLER LTD.	3.0
POLYMER CORPORATION LTD.	30.9
SHELL CANADA LTD.	6.1
SUN OIL COMPANY LTD.	5.0

Slide #8

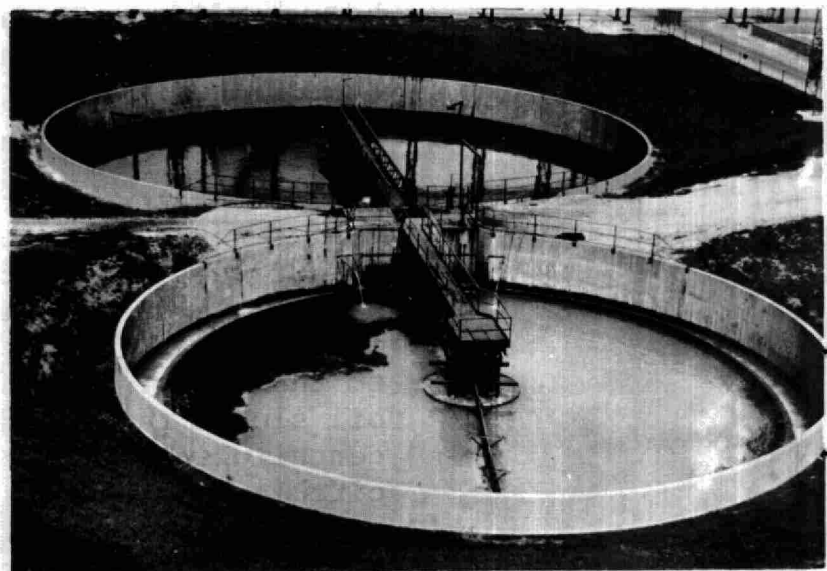


Slide #10

CAPITAL EXPENDITURES FOR
WATER POLLUTION CONTROL AND ABATEMENT

<u>YEAR</u>	<u>EXPENDITURE</u>
1986	\$42,000
1987	704,000
1988	733,000
1989	971,000
1990	715,000
1991	339,000
1992	306,000
1993 (ESTIMATED)	340,000
TOTAL	\$3,003,000

Slide #9



Slide #11

skimmers in detail. Phenols and oil contents of total effluent to the St. Clair River from this refinery now approximate 40 ppb and 6 ppm respectively.

2. Polymer Corporation Ltd. -

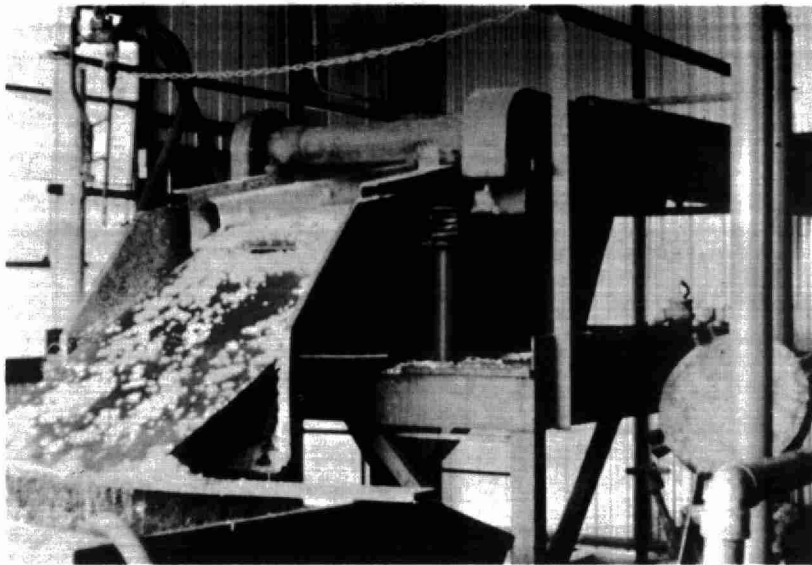
The major product of this company is synthetic rubber, which can constitute a major water pollution problem particularly when it is being handled in the latex state. The principle applied to latex waste streams is one of chemical coagulation prior to separation. The next slide (Slide #12) shows rubber leaving a vibrating screen and entering a Dempster bucket after having been coagulated from waste water with calcium chloride. The effluent water from this operation, in turn, goes to the large separator shown in the next slide (Slide #13). Residence time in this vessel is 1.5 hours, with the effluent water then being discharged to the sewer system. Skimmings from this separator are removed in Dempster buckets and buried. Monies expended on these systems in the last 8 years have exceeded \$300,000.

3. Sun Oil Company Ltd. -

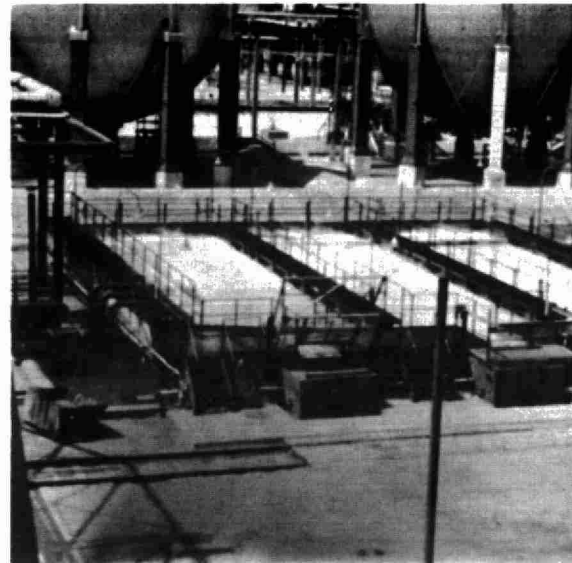
This refinery, situated south of Polymer and Dow Chemical Company, has chosen the biological oxidation route for phenol disposal. Part of these facilities are shown in the foreground of the next slide (Slide #14) with the refinery proper in the background. This installation is a typical bio-oxidation unit, employing sulphide stripping of feed water, a process water separator, aeration tank, shown in the next slide (Slide #15), clarifier, and sludge recirculation. Phenol concentrations in combined effluent water to the St. Clair River approximate 40 ppb.

4. Ethyl Corporation of Canada Ltd. -

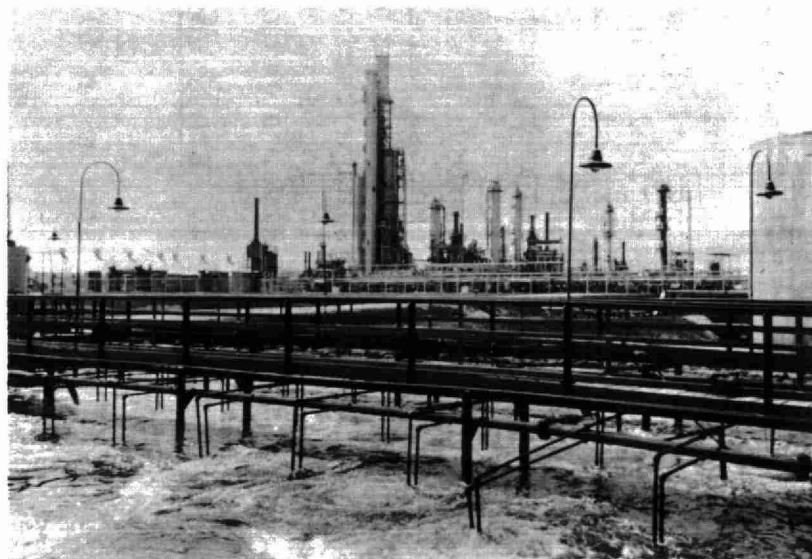
This 12 million dollar plant, which came on stream in 1956, manufactures tetraethyl lead,



Slide #12



Slide #13



Slide #14



Slide #15

ethyl chloride, and ethylene dichloride. The waste water facilities shown in the next slide (Slide #16) were installed during initial construction at a cost of \$500,000. They incorporate a duplicated rotational system of settling, acidification, and clarification, designed to maintain lead concentrations in total plant effluent at levels consistent with drinking water clarity. Additional details on this plant are available from the paper presented by Mr. L. A. Robb to this conference in 1962.

These are only some examples of the water pollution abatement facilities installed by those industries located along the St Clair River. Again I would reiterate that total expenditure during the past 8 years has exceeded \$5,000,000.

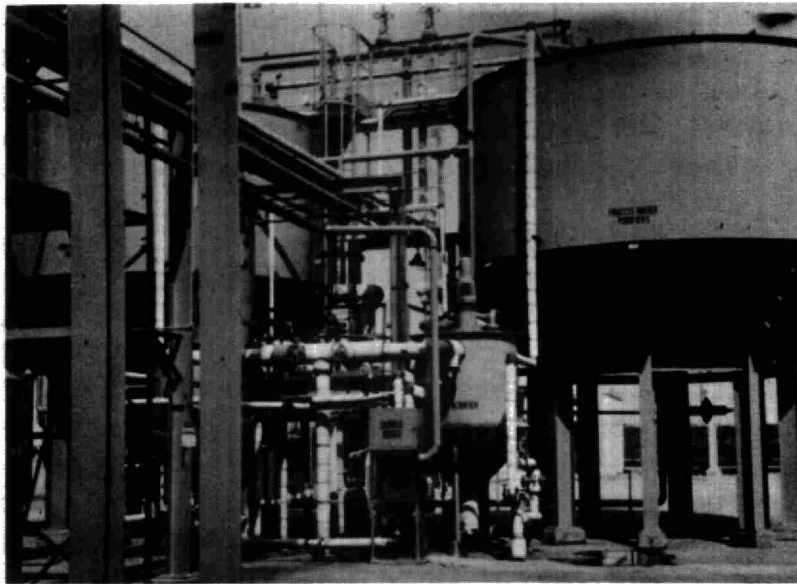
RIVER WATER QUALITY

What has been the effect of these expenditures on the overall quality of the St. Clair River? Two main quality criteria are available which are considered valid for such an assessment, viz:

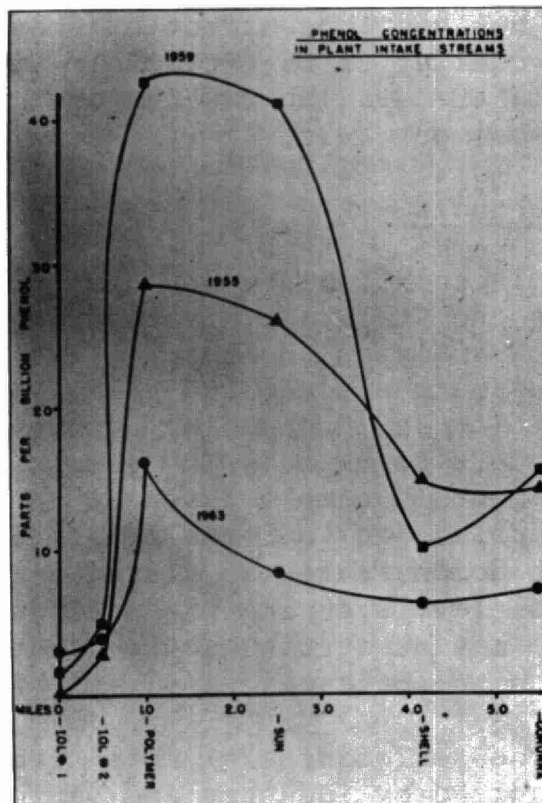
1. Phenols -

Since 1955 all major companies situated along the St. Clair River have performed regular phenol analyses on their intake waters as shown in the next slide (Slide #17). The various plant intakes proceeding downriver are shown from left to right. The sample from Corunna is a monthly sample taken downstream of these industries and analyzed by all companies. The graph demonstrates an alarming increase in phenol levels during the period 1955-1959 which may be attributed to general industrial growth in the area.

The seriousness of this situation was recognized by industry and various corrective



Slide 16



Slide 17

measures (as noted above) were initiated. The success of these measures is obvious from the curve shown for 1963, where phenol concentrations at all measurement stations have been markedly reduced to well below the 1955 levels.

2. Biological Surveys -

In 1957, 1959, and 1963 the St. Clair River Research Committee engaged the services of consulting biologist, Mr. T. W. Beak, of Kingston, Ontario, for the purpose of conducting surveys to determine the extent and degree of pollution in the St. Clair River. These surveys covered the whole river from north of Sarnia to Port Lambton on both the American and Canadian sides (Slide #18). (See Slide 2)

In measuring pollution Mr. Beak made use of the fact that different types of bottom living organisms have different levels of toleration to pollution and applied this fact to the analyses of several hundred river bottom samples. Details of this method have been recently published in Volume 60 of Chemical Engineering Progress, January 1964. Mr. Beak arrived at the following conclusions from the 3 Sarnia surveys:

- (a) Pollution takes place immediately downstream of the various Sarnia industries due to the nature of their waste discharges.
- (b) This pollution, or biological degradation, is restricted to a narrow strip of water (100') close to the Canadian bank and does not extend to the U. S. side of the river. In actuality, Mr. Beak has estimated that the significantly affected part was only about one-twelfth of the width of the river and about one fiftieth of the water volume.
- (c) There is progressive recovery downstream from Corunna as the narrow strip of

affected water widens and becomes progressively more diluted. Conditions at Port Lambton are relatively unpolluted.

- (d) The river has reacted favourably to reduction in pollution load by some member companies in spite of industrial expansion during the 1957-63 period.

CONCLUSION

In conclusion, I believe that significant progress in water pollution control has been and will continue to be made in the Sarnia area. The "Committee" approach to pollution abatement has been highly successful in providing a guide to industrial management for the installation of control facilities. Sarnia management in turn and on a voluntary basis has used this guide effectively in spending more than five million dollars on such equipment in the past 8 years.

SESSION THREE



G. U. Proctor
Proctor & Redfern
Session Chairman

"WASTE WATER CONTROL FOR A
MODERN STEEL FINISHING MILL"

by

C. D. HARTMAN

INTRODUCTION

Expansion in steel making and finishing capacity elsewhere in the world has been outstripping corresponding growth in the United States. While we are still able to maintain leadership in this major industry, the increasing number of new installations and the availability of low cost labour in other lands are threatening this position. Still other pressures are being exerted by domestic metal, glass, and plastic industries.

To fight back, steel is building new modern facilities and retiring old inefficient facilities. By speeding up production, automating certain operations, improving product quality, and producing new marketable items, new plant construction is required. In nearly every such case, local authorities are requiring the installation of adequate wastes control facilities to satisfy the increasing need for the protection of the water resources in the area. Steel plants, such as the plant of Midwest Steel, a division of National Steel, on the shore of Lake Michigan, accepted the financial and moral obligation of waste water control.

DEVELOPMENT AND OPERATION OF FINISHING MILL

The site of the new mill at the southernmost tip of Lake Michigan is adjacent to Burns Ditch. Figure 1 is a photograph of the unimproved site - an area within the belt of the Indiana Sand Dunes which is now the object of special interest groups to conserve its natural beauty.

National Steel Corporation first acquired the land in 1929, and thirty years later, it was used for the construction of the Midwest Finishing Mill. Figure 2 shows the completed mill which produced galvanized steel as early as December, 1960.

The finishing mill operations are identified in Figure 3, and may be referred to in tracing the travel of steel in the Midwest plant. Hot rolled coils produced by the new 80-inch hot strip mill at Great Lakes Steel, a sister division near Detroit, are shipped to Midwest. Steel is first pickled at the 80-inch continuous pickling line, using a solution of sulphuric acid, and then the coils are reduced in gage by cold rolling of the 5-stand tandem mill. After cold working, annealing and tempering of the strip may be required. For final finishing, a protective coating may be applied by continuous galvanizing or by electrolytic tinning. The tin temper mill, normally used to toughen the surface of the steel, is also used to reduce tin plate to very thin gages.

PLANNING FOR WASTE WATER CONTROL

As soon as a public announcement was made of the new mill, a sampling program was initiated to evaluate the quality of the water adjacent to the plant site. The water survey was organized for examination of samples of water collected periodically at various points in Burns Ditch and in the lake. The survey information provided valuable data for selecting the location of the lake water supply intake, as well as establishing a reference for general water quality of the region before starting any mill construction.

Local, state, and federal authorities were consulted as early as possible to learn what regulations, or limitations, may have bearing upon the utilization of water by the mill. Among the Government groups frequently consulted were the Porter County Zoning and Planning Board, the U. S. Corps of Engineers, the State of Indiana Conservation Department, Flood Control and Water Resources Commission, and the Water Pollution Control Board. Indiana regulations and laws





Figure 2

Midwest Steel Division Product Flow Chart

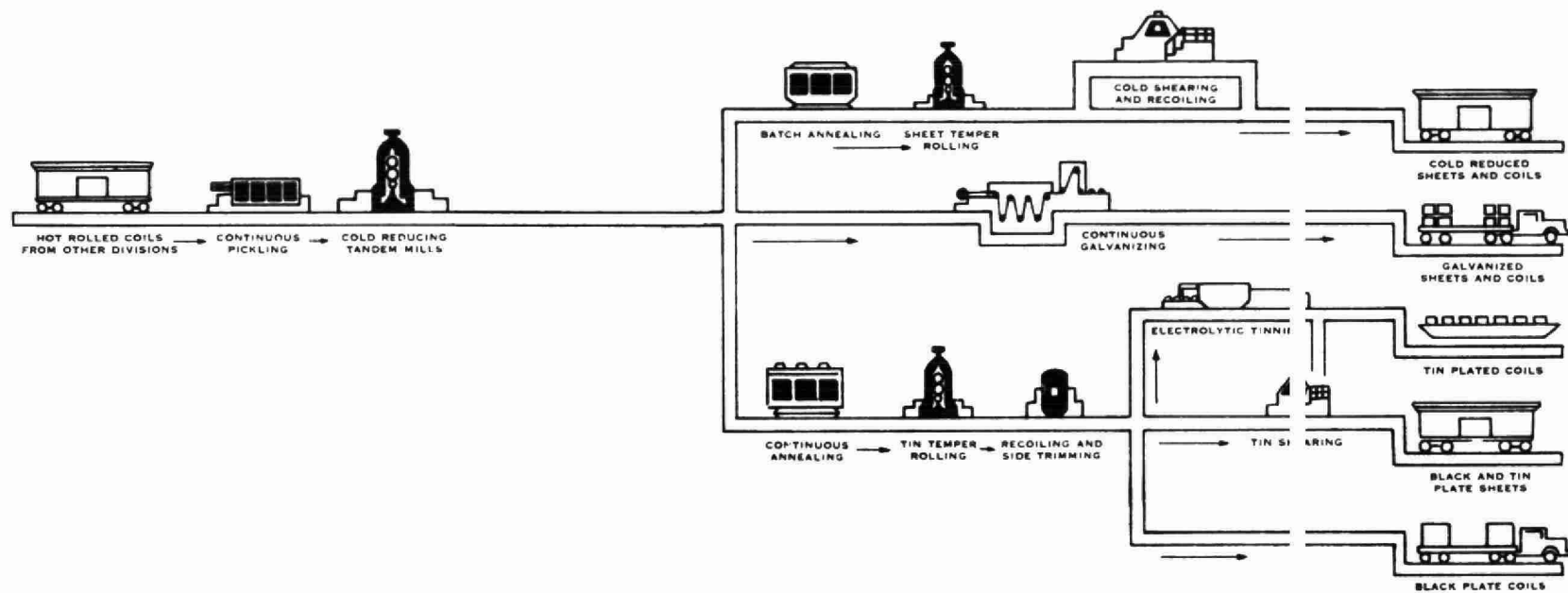


Figure 3

stipulate limits of permissible discharge of certain waste substances, which are known to be common to most domestic and industrial activities. In addition, the Water Pollution Control Board considers each potential waste water discharge on an individual basis to determine what effect it may have on water quality in the general area or how it may influence any subsequent uses of the water. It was necessary to meet regularly with members of the Water Pollution Control Board during the initial stages of planning in order to inform them of contemplated operations in the mill and to have guidance in establishing a proper waste water control program.

The mill and its personnel produce many waste products, eventually becoming water-borne, which require treatment before disposal. Sanitary sewage contributed by a mill population of 2,000 persons involves control measures for biochemical oxygen demand, dissolved oxygen, suspended solids and floating material. Waste water from mill operations conveys additive materials including pH depressants, suspended solids, floating and soluble oils, color inducing substances, iron, tin, zinc, chromium and fluoride. The concentrations of all of these products have to be controlled to within acceptable limits before releasing any water to Burns Ditch. It soon became evident that acceptable control could not be provided effectively by one central facility treating all waste flows together, no matter how appealing it might be for initial cost and ease of operation.

Each of the major contaminants had to be studied to determine what waste flows at the mill could be combined and conveyed together in an industrial waste sewer system for combined treatment, and which waste flows had to be kept segregated for individual treatment. With this analysis completed, overall planning could begin by considering equalization of waste water flow rates and varying concentrations, the proper staging of step treatment, design criteria for treatment processes, the elimination of pumping trunk sewer flows and, finally, concentrating the waste water control facilities in as few sites as possible.

At this point, a preliminary engineering report and general plans outlining the waste water control facilities were prepared and submitted for consideration by the Water Pollution Control Board. The comments and suggestions of the Board representatives were helpful in establishing certain objectives of the waste water control program. Later, final designs were reviewed and approved by the Board before construction of any facility was started.

The general plan included, as the first step, the separation of clean cooling water into the storm drainage system for direct discharge. Second, all compatible flows collected in the industrial wastes sewer could be treated jointly at a single chemical treatment plant. Waste water flows such as caustic cleaning rinse water and dumps, pickling acid rinse water, most floor drain sump discharges, various blowdowns and certain pretreated flows are combined. In all, about 25 different waste streams are collected in the industrial wastes sewer. Third, the remaining non-compatible flows are conveyed separately to industrial wastes pretreatment areas, consisting of three individual oily wastes streams, a chromium system, a fluoride system, and a waste pickle liquor collection system.

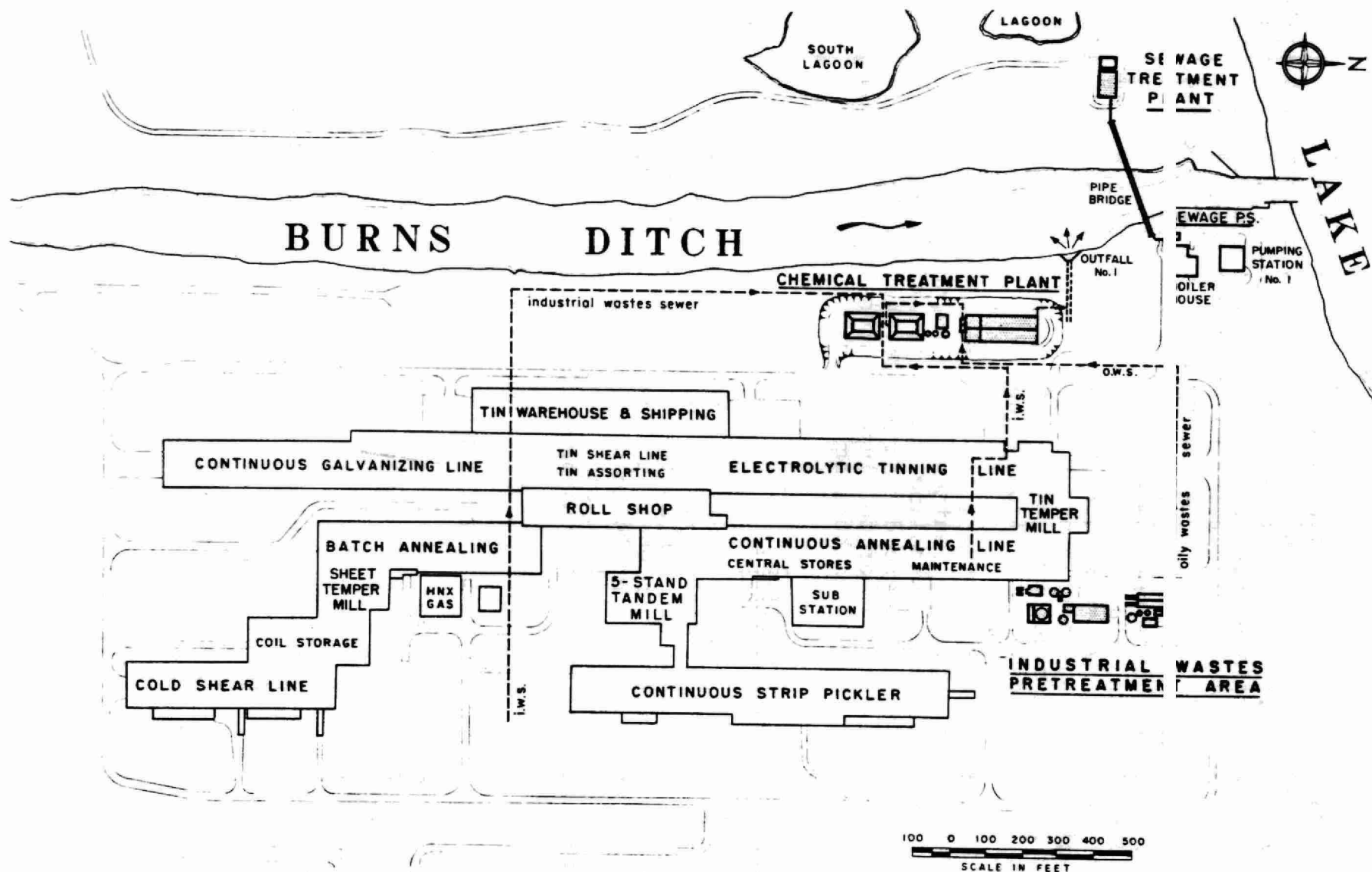
Figure 4 shows the sites selected for the treatment facilities. The pretreatment area is located just east of the continuous annealing building. After proper pretreatment, the flows are discharged to the combined industrial wastes sewer, or to sludge disposal. The various sludges are disposed of in holding lagoons.

SEWAGE TREATMENT FACILITIES

Sanitary sewage is separately collected in a cement-lined cast iron pipe system and is delivered by gravity to a pumping station at the east bank of Burns Ditch. The sewage is pumped in a force main over a utility bridge to the west side of Burns Ditch to the sewage treatment plant. These facilities can be seen in relation to the steel mill buildings in photograph, Figure 5.

The sewage treatment plant shown in photograph, Figure 6, is now designed to treat a flow of 330,000 gallons per day and can ultimately be expanded to handle 640,000 gpd. The treatment process incorporates the latest developments in activated sludge treatment and aerobic digestion of sludge. The final innocuous sludge is disposed of in a sludge lagoon. Figure 6A is a schematic representation of the sewage treatment process.

The process provides a reduction of 95 per cent BOD and 90 per cent removal of suspended solids. The final effluent is chlorinated and returned to Burns Ditch in a 24-inch outfall sewer. We are presently operating with a 5-day BOD of 2 to 4 ppm and suspended solids of 5 to 10 ppm in the final effluent.



LOCATION OF WASTES TREATMENT FACILITIES
WASTE WATER CONTROL AT MIDWEST STEEL

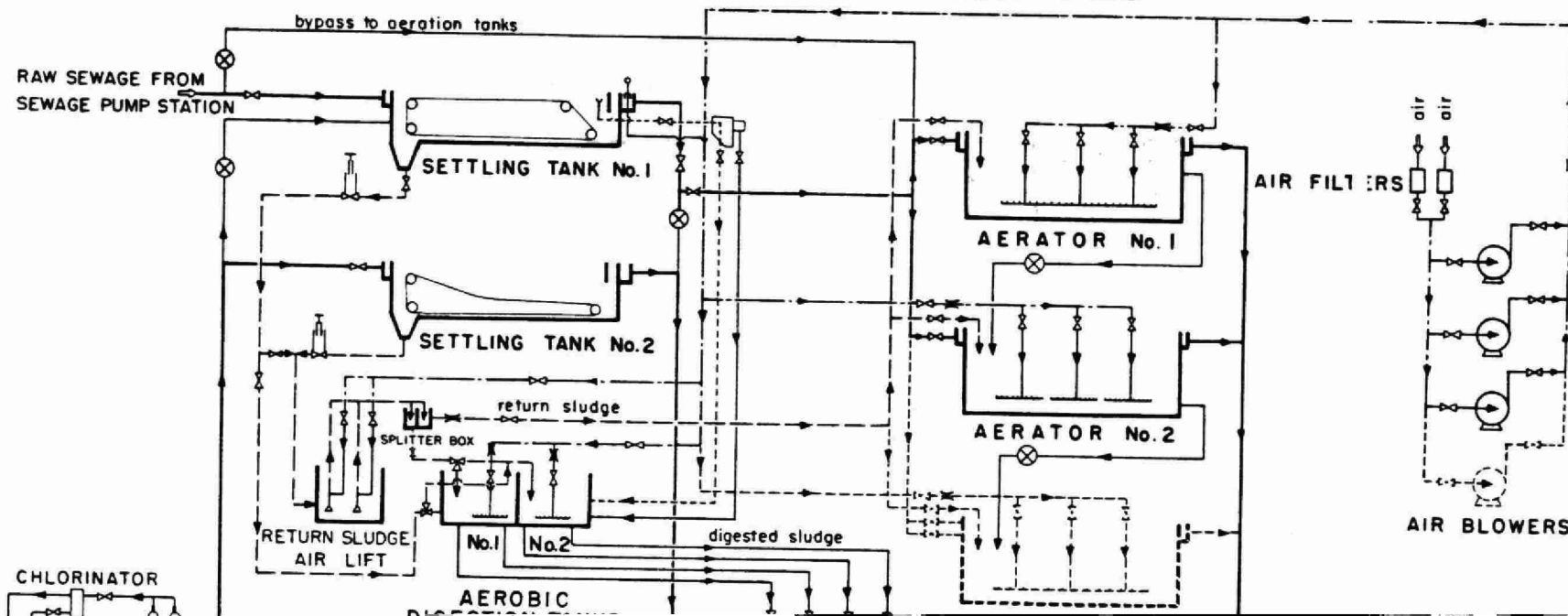
Figure 4





Figure 6

SCHEMATIC FLOW DIAGRAM SEWAGE TREATMENT PLANT WASTE WATER CONTROL AT MIDWEST STEEL



CHEMICAL TREATMENT PLANT

The chemical treatment plant is located along the east bank of Burns Ditch, approximately 1,000 feet from Lake Michigan. Figure 7 shows the location of this waste water control facility. The chemical treatment plant provides final treatment by coagulation, oxidation, flocculation and sedimentation for the numerous flows collected by the industrial wastes sewers and the various pretreatment plant effluents.

Figure 7A is a simplified diagram showing the collection system for discharges from the various mill operations and pretreatment facilities, as well as how these flows are clarified in the chemical treatment plant.

The hydraulics of the collection system and the flow through the treatment plant were carefully worked out to avoid the installation of pumping stations. This was accomplished by constructing the chemical treatment plant in a depression some ten to twelve feet below mill grade. Because of this, most of the treatment units had to be constructed below the ground water table. It was then necessary to provide a subdrain well system in order to control uplift pressures whenever a treatment unit was being dewatered.

All major waste flows discharge initially into equalization basins. The incoming flow is distributed in the basins and retained to equalize flow variations, and also to blend and pre-mix the different types of wastes. Since the dominant characteristic of the combined waste is acidic, the equalization basins have a protective coating as well as limestone backfill around the influent distribution channel in the basin. Diffused air keeps the wastes agitated, and also helps to satisfy the oxygen demand exerted by the ferrous iron in acid rinse water from the pickling operation. Oil skimming is also performed in corners of the basins.

The flow, leaving the equalization basins, enters the mixing tanks where separan, lime, and acid may be added for coagulation and pH control. Air is again induced to help agitate the flow and to complete oxidation. Two mixing tanks can be used in series or individually, and after mixing, the flow enters and is distributed across the flocculation sections of each of two treatment tanks.

Following a 20-minute minimum period of flocculation, the flow passes directly into the sedimentation area. Each sedimentation tank is equipped with a longitudinal sludge



Figure 7

SCHEMATIC FLOW DIAGRAM CHEMICAL TREATMENT PLANT WASTE WATER CONTROL AT MIDWEST STEEL

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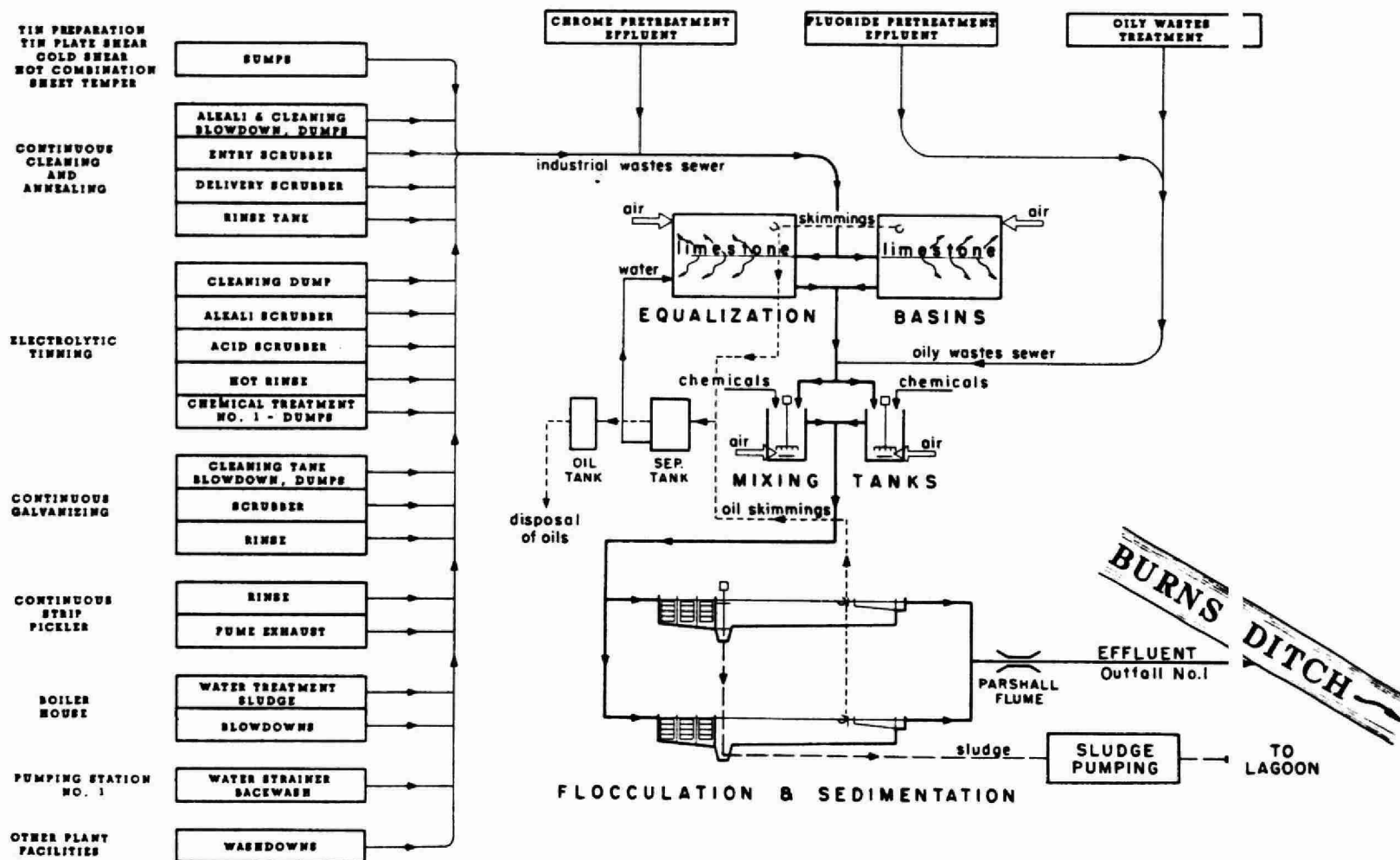


Figure 7A

collecting mechanism, a cross collector and a sludge draw-off pipe leading to the wet wells of the sludge pumping station at the control building. Oils and scum are removed at the effluent end of each tank by a transverse surface pipe skimmer, drained by gravity into a sump, and then pumped to an oil separator tank for concentration. The treated plant effluent flow is measured by a Parshall flume before being discharged to Burns Ditch.

The average flow of the chemical treatment plant is approximately 4,000 gallons per minute and can ultimately be increased to 16,000 gpm as more mill facilities are added. The effluent from the chemical treatment plant is the main discharge from the finishing mill facilities.

ACID NEUTRALIZATION

Acid neutralization is the first to be described of the different facilities shown in Figure 8, a photograph of the industrial wastes pretreatment area. The dominant acid to be neutralized is sulphuric acid in the waste pickle liquor overflow from the continuous strip pickler. In addition to this flow directed to the acid neutralization plant, are pickling tank dumps and chromic acid dumps from the electrolytic tinning line and from the continuous galvanizing line.

The waste pickle liquor to be treated contains from 6 to 8 per cent sulphuric acid and 16 to 18 per cent ferrous sulphate. The pH of waste pickle liquor is less than 1.0 and its temperature may be as high as 190°F when discharged from the continuous strip pickler. The daily volume of waste pickle liquor is approximately 60,000 gallons.

The waste pickle liquor from the continuous strip pickler is pumped from the mill area in a polypropylene lined steel pipe. It first passes through a heat exchanger, as shown in figure 8A, to lower its temperature rise from a subsequent heat of reaction. The cooled waste pickle liquor then passes to the holding tank which has a storage capacity of 100,000 gallons. Other waste acids from mill operations are pumped directly to the holding tank. The chromium in the chromic acid dumps is reduced by the waste pickle liquor in the holding tank and later precipitated during neutralization. Waste pickle liquor is also used for coagulating, chromium reduction, and de-emulsifying wastes in nearly every facility in the industrial wastes pretreatment area as well as in the chemical treatment plant.

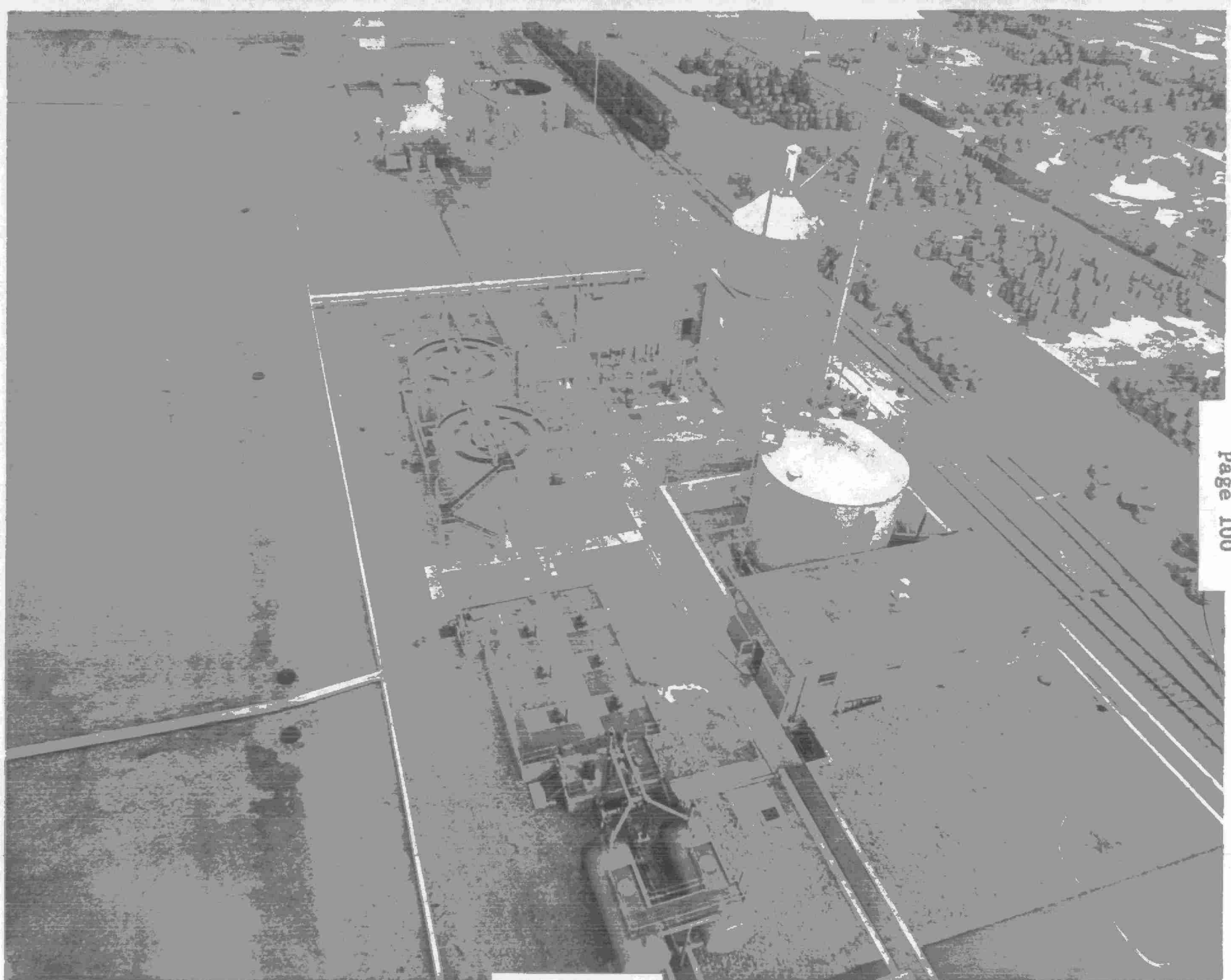


Figure 8

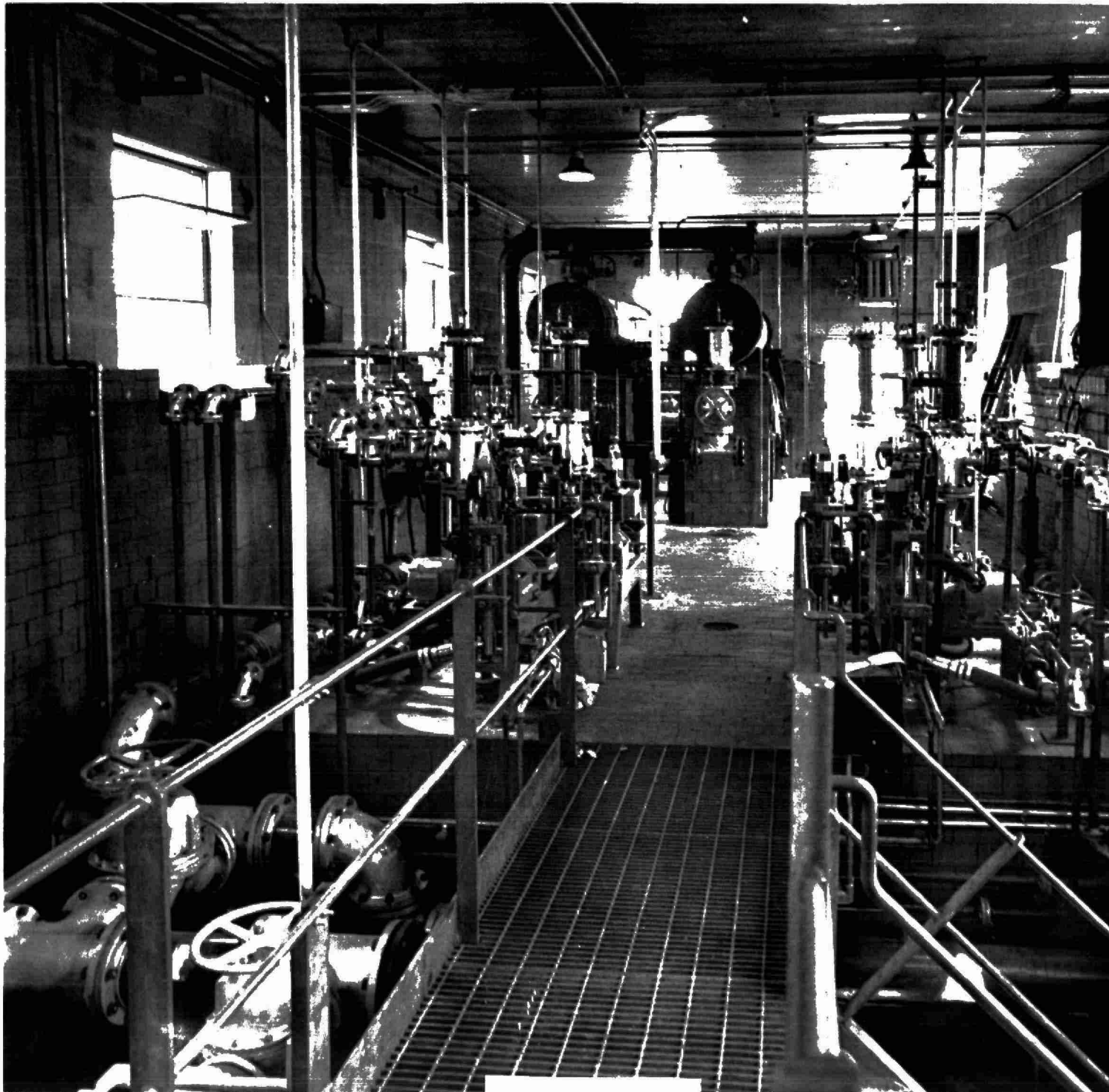
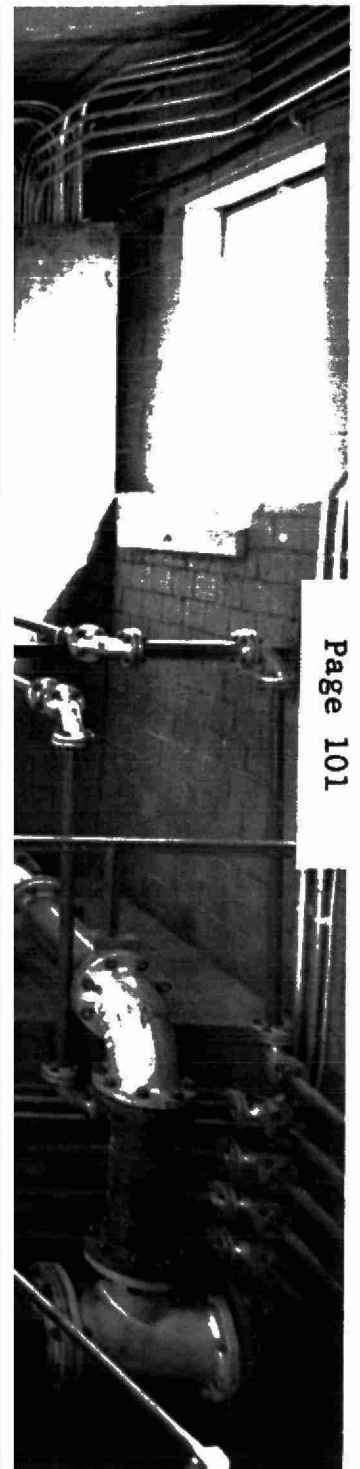


Figure 8A



Neutralization of waste pickle liquor is carried out at a constant pre-set rate of flow by means of a magnetic flow meter and a control valve. By-product lime from acetylene production is used as the neutralizing agent. Facilities are installed to feed lime either as a fine dry hydroxide powder, or as a lime slurry to the rapid mixing tanks. We prefer to use lime slurry. The rate of lime feed is controlled and adjusted by pH measurement of the effluent from the neutralization process. After the addition of lime, the liquor is held for a period of 30 minutes or more, in a reaction tank, before discharging to the wet well where air operated sludge pumps pump the neutralized sludge to the holding lagoons. The neutralization process may be followed on the flow diagram presented in Figure 8B.

A bucket elevator and screw conveyor unload the lime from railroad cars to an overhead lime storage bin having a capacity of 170 tons. Below the bin, two belt-feeders and lime slurry mixer tanks supply lime slurry to the wet neutralization process. In addition, other lime slurry tanks and feed pumps are installed to provide lime slurry for other treatment processes in pretreatment area. The neutralization facilities are shown in photograph, Figure 8C.

OILY WASTES CONTROL

In our present phase of steel finishing at Midwest, the 5-stand tandem mill and the operation of the tin temper mill for double-reduced tin plate, produce as great a variety of oily wastes as will be discharged by all the mills we might ultimately install. Therefore, some nominal capacity for each type of oily wastes control facility had to be built immediately. These facilities are located in the industrial wastes pretreatment area.

The 5-stand tandem mill is versatile and produces tin plate, galvanize sheets and mill clean black plate by cold working. When the mill is on tin plate or light gages of galvanize, an oil recirculation system is used to lubricate as well as cool the strip. The system recirculates a rolling solution of 10,000 gallons made up with about 1,000 gallons of emulsifying oils and bacteriocidal agents added. By straining, cooling, conditioning and adding makeup to the solution, it may be reused for seven to ten days. When the solution is considered spent, it is dumped to the oily waste pretreatment area, and a fresh solution of 10,000 gallons is substituted. When the mill is on

SCHEMATIC FLOW DIAGRAM ACID NEUTRALIZATION

WASTE WATER CONTROL AT MIDWEST STEEL

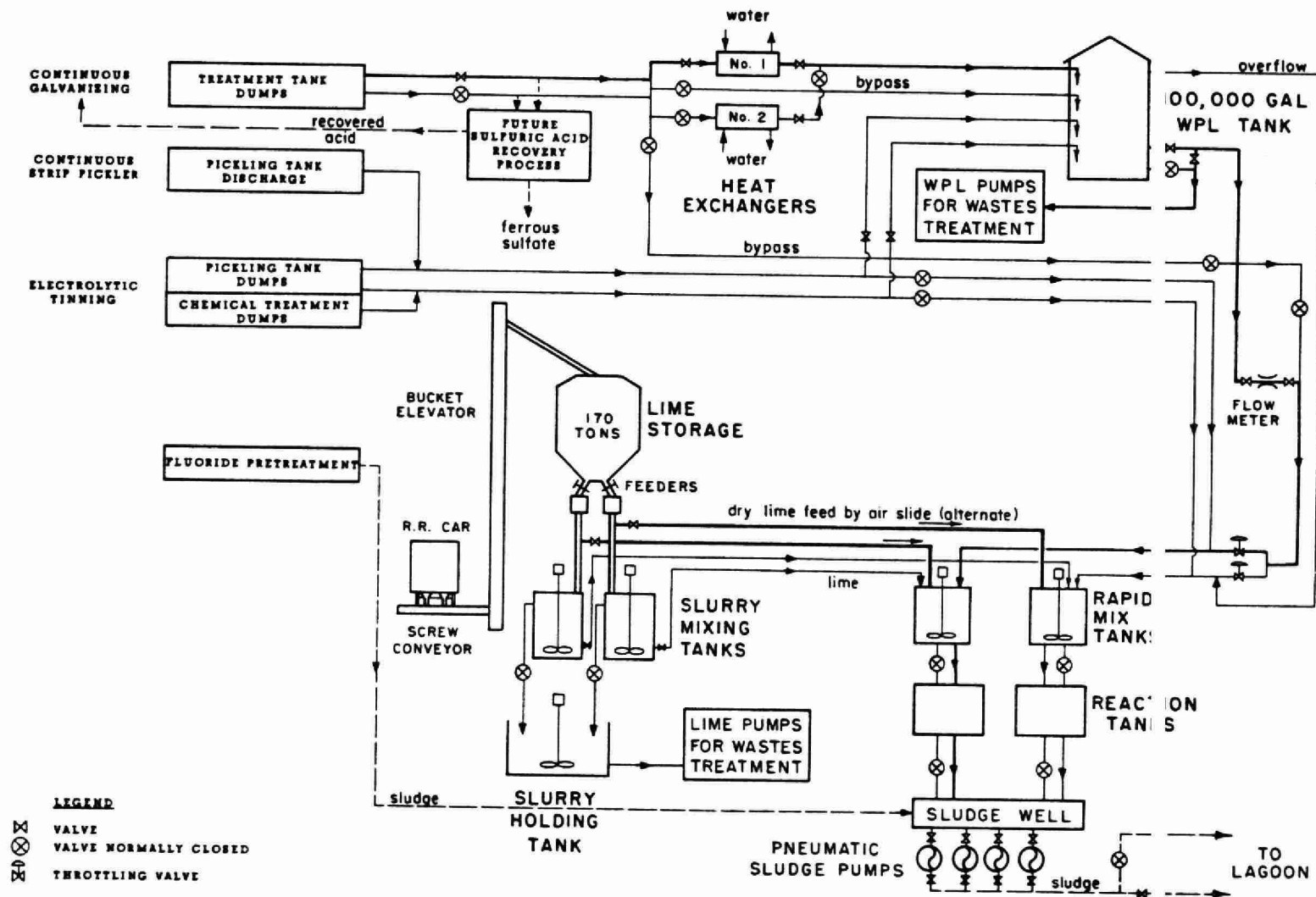


Figure 8B



Figure 8C

heavy gages of galvanize or mill clean black plate, some of the stands use a direct method of solution application. In this case, lubricant and water are applied to the stand only once and discharged directly to a sewer. The flow entering the sewer contains approximately 200 ppm of oils, and the rate of flow may reach a maximum of 6,000 gpm.

The oils discharged for treatment may be of mineral, animal or vegetable origin, soluble or insoluble, and may be found in different degrees of being free or emulsified, saponified or unsaponified.

The tin temper mill is operated in a manner similar to the 5-stand tandem mill when double-reduced tin plate is produced. However, since only two stands are involved and reductions are nominal, the rate and amount of oil and water use are much lower. The average flow is from 100 to 150 gpm, but may have an oil content in the range of a thousand parts per million.

In addition to the waste flows from mill operations, other oily wastes are generated by washdowns and fog eliminator sluicing. To cope with all of these variable in volume, in oil content, and in characteristics, it is necessary to provide control facilities of at least three general types. The wastes can thereby be directed to the proper receiving unit and processed progressively to obtain a lesser oil concentration in the larger volumes of water and a greater oil concentration in the smaller volumes of water. The three types of facilities are:

1. Oil interception - for large water volumes with low oil content.
2. Oil separation - for moderate water volumes or oil content
3. Oil concentration - for small water volumes having high oil content.

At each type of control facility, chemicals, air and heat, are added to help separate the oils from the waste water. Descriptions of these three facilities and flow diagrams explain how oily wastes are controlled.

OIL INTERCEPTION

The waste discharge from the direct method of rolling is pumped from a skimming tank at the 5-stand tandem mill, through a 24-inch steel force main, to an

equalization tank at the industrial wastes pretreatment area. Figure 9 shows the waste water control facilities at the oil interception plant.

The incoming flow is mixed and pre-skimmed in the equalization tank before passing to a mixing tank where it is joined with the treated water from the oil separation plant. At the mixing tank, waste pickle liquor may be added to lower the pH and assist in breaking oil emulsions prior to discharge to the interceptor tanks. Each oil interceptor tank has a volume of 66,000 gallons and provides a detention period of 20 minutes at its design flow of 3,300 gpm. Free oils, which float to the surface, are skimmed off at the effluent end of the tank and then pumped to the oil concentration plant. Solids settling to the bottom are removed from the tank by a sludge collector mechanism which deposits sludge into containers at plant grade. The treated flow is gaged and is discharged to the industrial wastes sewer to be conveyed to the chemical treatment plant for a final step in treatment. The treatment process can be followed on the flow diagram, Figure 9A.

OIL SEPARATION

The chemical flocculation and dissolved air flotation process for separating oils is suitable for handling the moderate continuous flow from the fog eliminator and tunnel sluicing, the waste rolling solution from double-reduced tin plate and the water drawoff from oil concentration. The treatment units are housed at the north end of the general operations building near the oil interception facilities and are shown in Figure 10.

All waste flows enter a primary holding tank where free oils and solids are separated. The skimmed oils are pumped to the oil concentration facilities and the solids to oil interception. The effluent from the primary holding tank contains suspended emulsified oils which are treated with waste pickle liquor, lime, and air, and then are pumped to a retention tank to allow reactions and dissolution of air to be completed. The treated flow is then released into a flotation tank where the coagulating chemicals form a floc and the entrained air under reduced pressure forms tiny air bubbles. The floc and air bubbles rise upward and carry suspended oils to the surface. The flotation tank is designed for an overflow rate of 2 gpm per square foot at a flow of 250 gpm. The clarified water is discharged to the oil interception tanks. Figure 10A presents the schematic flow diagram for oil separation.



Figure 9

SCHEMATIC FLOW DIAGRAM OIL INTERCEPTION PLANT

WASTE WATER CONTROL AT MIDWEST STEEL

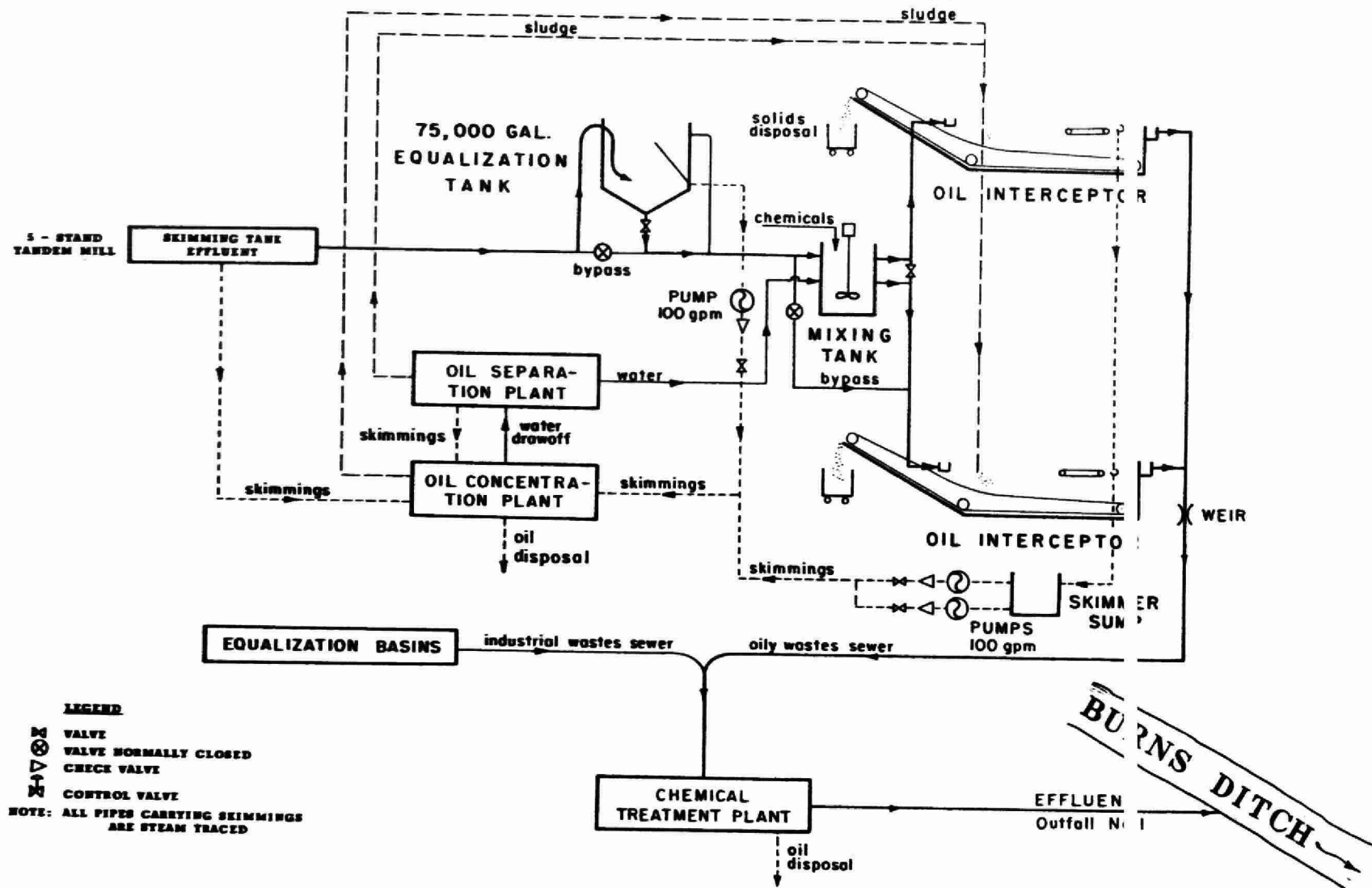


Figure 9A



Figure 10

SCHEMATIC FLOW DIAGRAM OIL SEPARATION PLANT WASTE WATER CONTROL AT MIDWEST STEEL

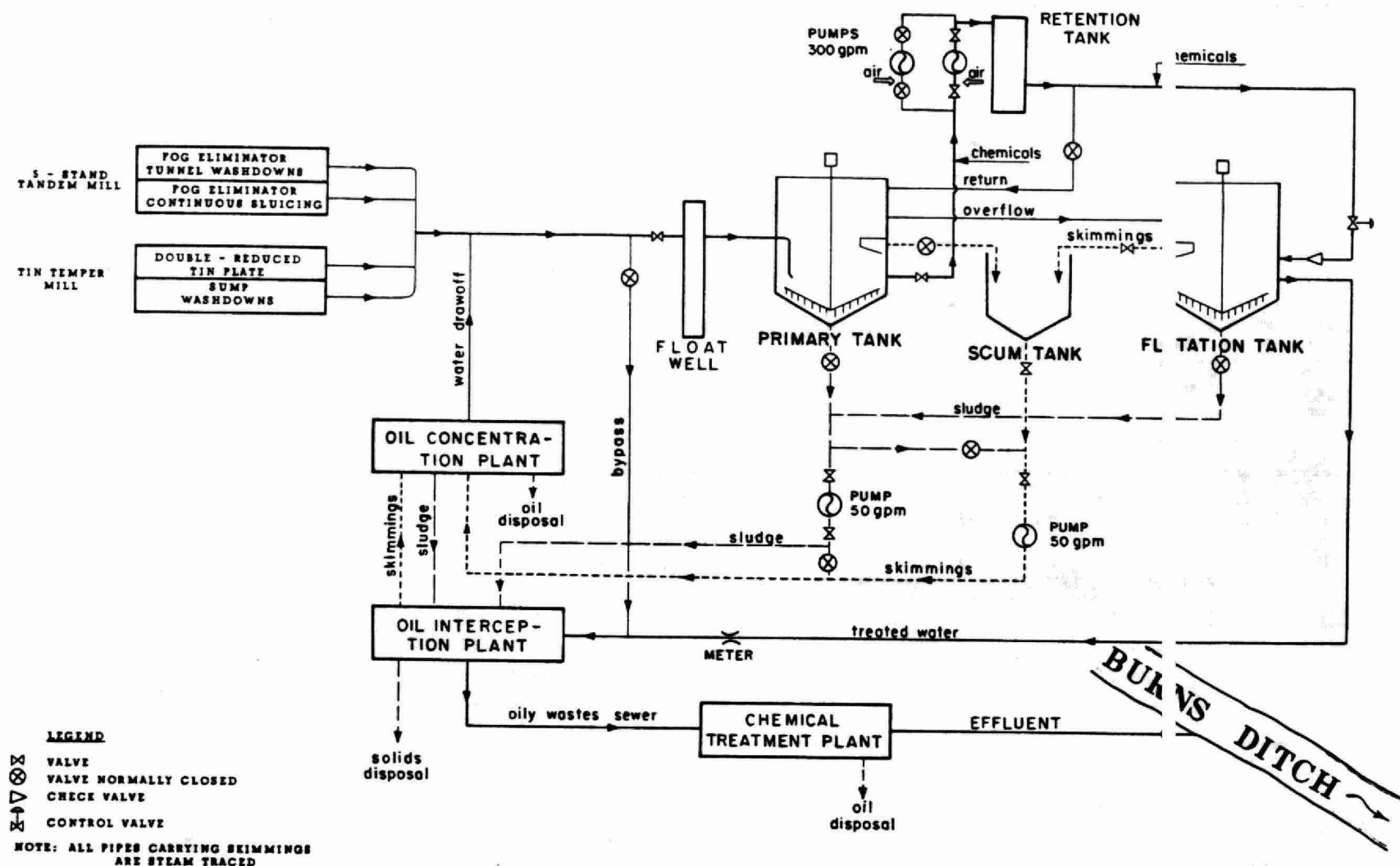


Figure 10A

OIL CONCENTRATION

Spent rolling solution, blowdowns, and similar concentrated oil wastes are pumped in a steam traced force main to an oil concentration tank. Heat is added to the insulated oil holding tank to further separate water and concentrate the oil. The water drawoff from the holding tank is pumped to oil separation primary holding tank, and settleable solids are pumped to oil interception. The skimmed oils are drawn to the oil storage tank. Further oil concentration occurs in the heated oil storage tank before final disposal of collected oil by trucking.

The oil concentration tanks and facilities are adjacent to the oil interceptor tanks as shown in Figure 11. Most of the oil, water and sludge pumps used in oily wastes control are installed in a separate, small pump house. The transfer of these substances is outlined in Figure 11A for the oil concentration operation.

CHROMIUM WASTES CONTROL

The chromium wastes pretreatment facilities are located in the industrial wastes pretreatment area just to the east of the tin temper mill as shown in figure 12. Chromium compounds, in the hexavalent form, are used for chemically treating finished product at the electrolytic tinning and galvanizing lines. After the coated strip leaves the chemical treatment units, rinse waters are applied to clean the strip of excess chemical. These chrome-bearing rinse waters are pumped to the pretreatment plant, and are treated by using the ferrous sulphate content of waste pickle liquor to reduce chromium to the trivalent form, which can readily be precipitated by adding lime.

The waste rinse waters are pumped from the operating lines to two equalization tanks located above plant grade where inflow rates and variations in concentration are equalized. The flow leaving the equalization tanks is metered and then enters a mixing tank where the waste pickle liquor is added. Approximately 30 minutes detention is provided in reaction tanks where mixing continues to permit the reduction process to be completed. The ferrous sulphate content of the waste pickle liquor acts as the reducing agent and the residual sulphuric acid of the liquor maintains an adequate level of low pH to promote complete reduction. Complete reduction of hexavalent chromium is measured by an oxidation reduction potential meter, with a 10 per cent excess of ferrous sulphate and a pH of about 2.5.

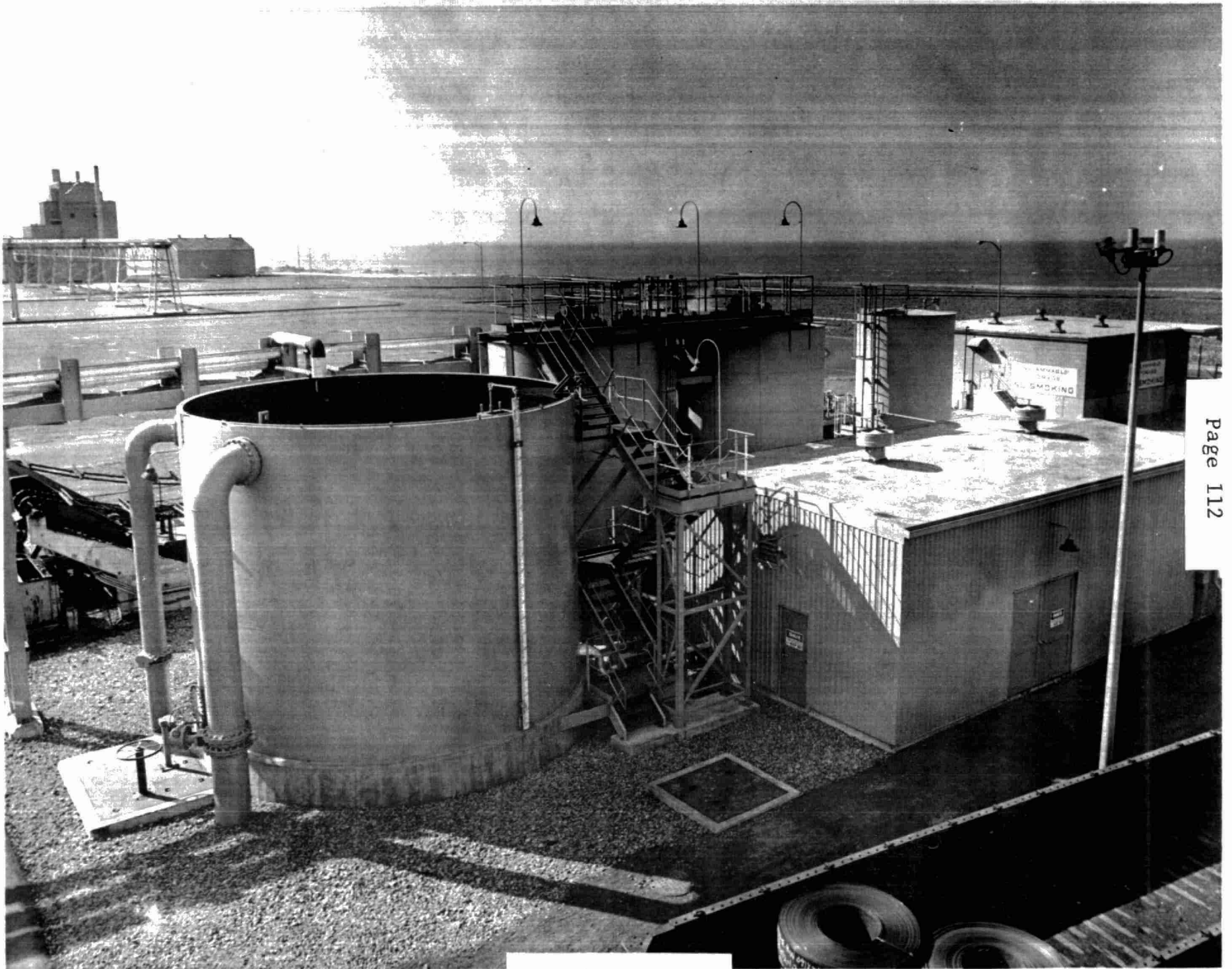


Figure 11

SCHEMATIC FLOW DIAGRAM
OIL CONCENTRATION PLANT

WASTE WATER CONTROL AT MIDWEST STEEL

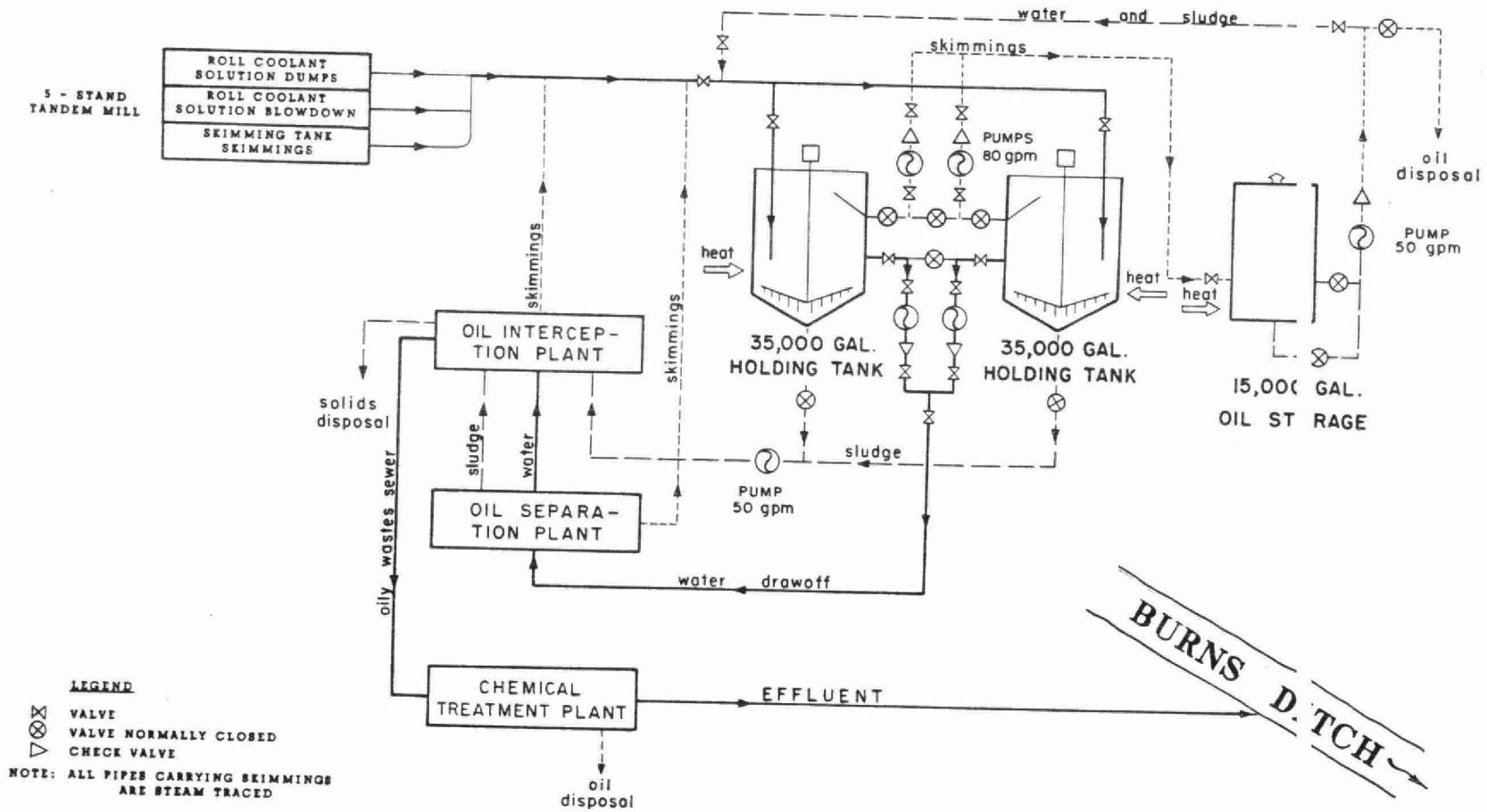


Figure 11A



Figure 12



The treated flow enters an effluent sump where lime may be used for pH adjustment for sewer conditions. Final application of lime at the chemical treatment plant neutralizes the acid condition and completes the precipitation of chromium hydroxide and ferric hydroxide. These sludges are removed from the sedimentation basins and pumped to the sludge lagoons. The process is outlined in Figure 12A.

FLUORIDE WASTES CONTROL

The electrolytic tinning line is the source of fluoride-bearing waste flows in the mill. The tin plating process used by Midwest is known as a "Halogen Line" in which a plating solution comprised of several reagents is used. Plating solution, which is a relatively expensive solution, contains Stannous tin, fluorides, chlorides, and Dupont agent No. 2.

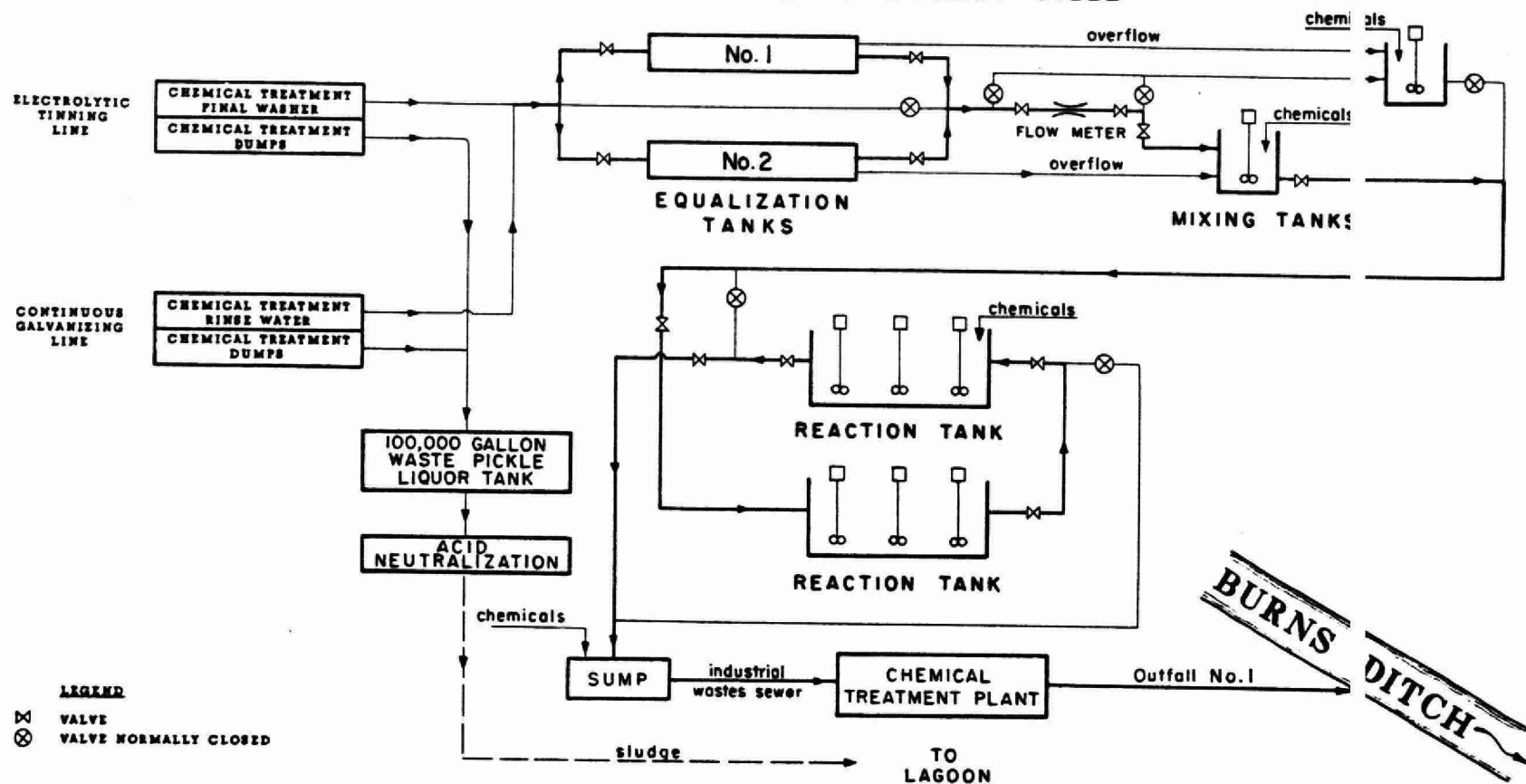
The plating process involves several preparatory steps before the strip enters a first level of plater cells where its underside surface is tinned. The strip travels vertically to a second level of cells where the top side is tinned. At a third level, the strip enters a reclaim tank where plating solution is recovered and the strip is rinsed before leaving the tank.

A series of final water sprays are used to remove small residual amounts of plating solution. The water used at the spray tanks is reused at a Plater fume exhaust washer, which discharges a flow of 125 gpm to a pretreatment reservoir. From this point, the waste water is pumped to the fluoride wastes treatment plant.

The final waste flow leaving the electrolytic tinning line contains small representative amounts of the plating solution, although the concentration of each contaminant will vary from time to time.

Since plating solution is valuable and contains high concentrations of substances of a critical nature to acceptable water quality, the mill was designed so that no possible discharge of solution to sewers could be made inadvertently. All plating solution sludges from periodic cleaning operations are collected, stored and processed in a separate sludge treating plant at the mill to extract all readily precipitable compounds for recovery, or disposal. Small waste water quantities from this process are also directed to the fluoride wastes treatment plant for further treatment.

SCHEMATIC FLOW DIAGRAM CHROMIUM WASTES TREATMENT WASTE WATER CONTROL AT MIDWEST STEEL



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Figure 12A

Facilities for treating fluoride wastes are shown in Figure 13. The flow is pumped from the mill to an elevated equalization tank, where surges in flow and variations in chemical composition are moderated. As the flow leaves the equalization tank, it is metered before entering a mixing tank, where measured amounts of lime and coagulants are added to the flow. The flow, after mixing, is subject to sludge recirculation, flocculation and settling in a circular reaction clarifier.

Lime is added in excess to drive the reaction between calcium and sodium bifluoride to completion within the retention period. This excess is also helpful in maintaining a ready supply of lime in contact with the waste to act as a buffer should equipment fail to operate properly and also to overcome any inaccuracies in feeding.

The reaction clarifiers are upflow type units which maintain a layer of sludge or blanket in the lower section of the tank. Clarified effluent is discharged to the industrial wastes sewer. The sludge accumulation is centrifuged and sold for its tin content. The process is outlined in the flow diagram presented on Figure 13A. Figure 13A does not show the centrifuge operation.

CONCLUSION

Industrial wastes treatment facilities, similar to those installed by Midwest Steel, are costly even in the case of a new plant, which can incorporate in the original planning all necessary piping, pumping, and treating units. For an old established plant, equal facilities would cost substantially more, and in some cases of overcrowded plant conditions, would be very difficult to provide.

Of great assistance in planning new facilities is the willing participation of stream pollution control officials in providing guidance, review and suggestions concerning a waste water control program. Their helpful co-operation extends from the initial phases of planning through the final consummation of approved designs.

As for the industrial plant, the expenditure of monies for waste control can be repaid only in the form of good public relations which may engender greater sales of its products and in the satisfaction obtained from doing a good job in conserving this increasingly important natural resource.

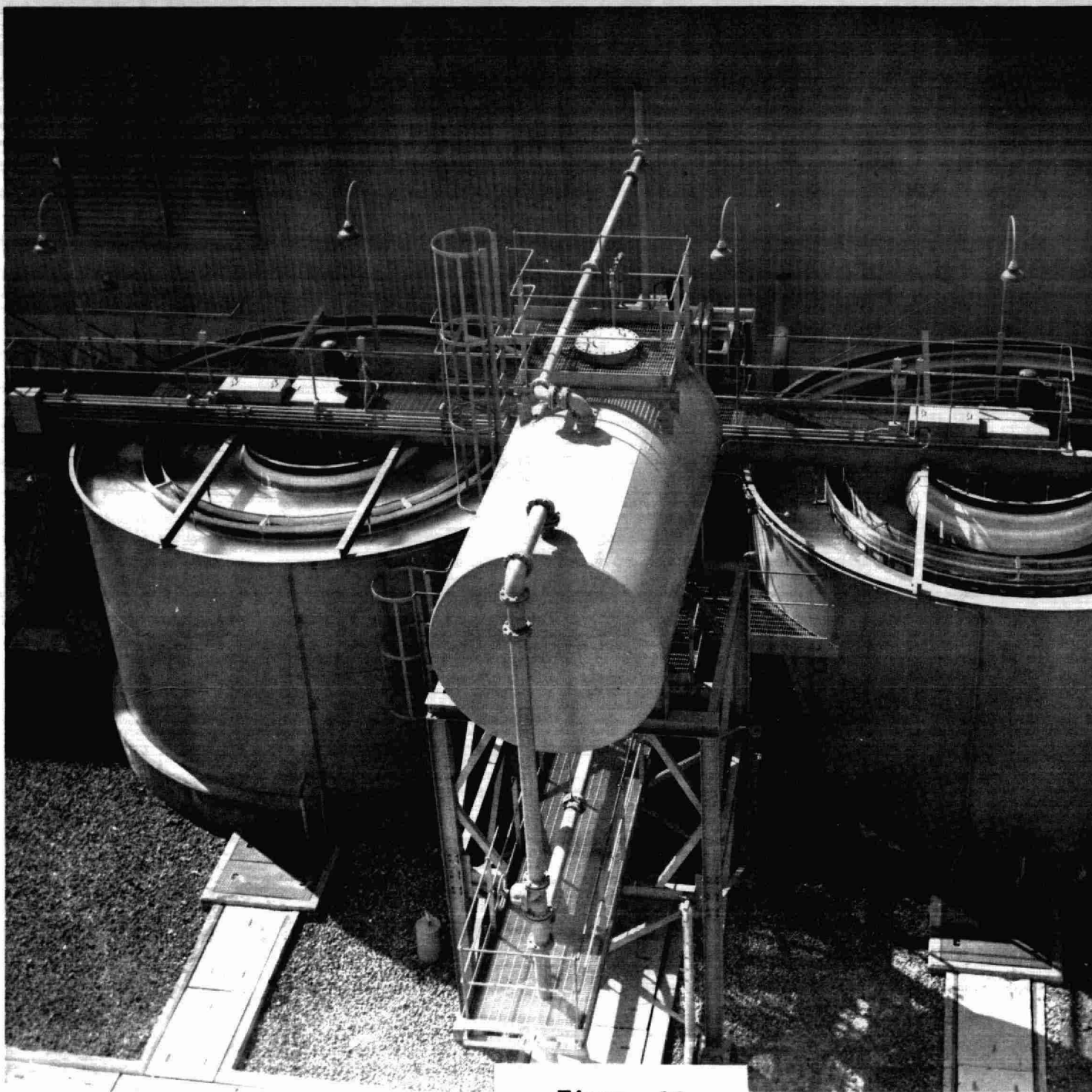


Figure 13

SCHEMATIC FLOW DIAGRAM FLUORIDE WASTES TREATMENT WASTE WATER CONTROL AT MIDWEST STEEL

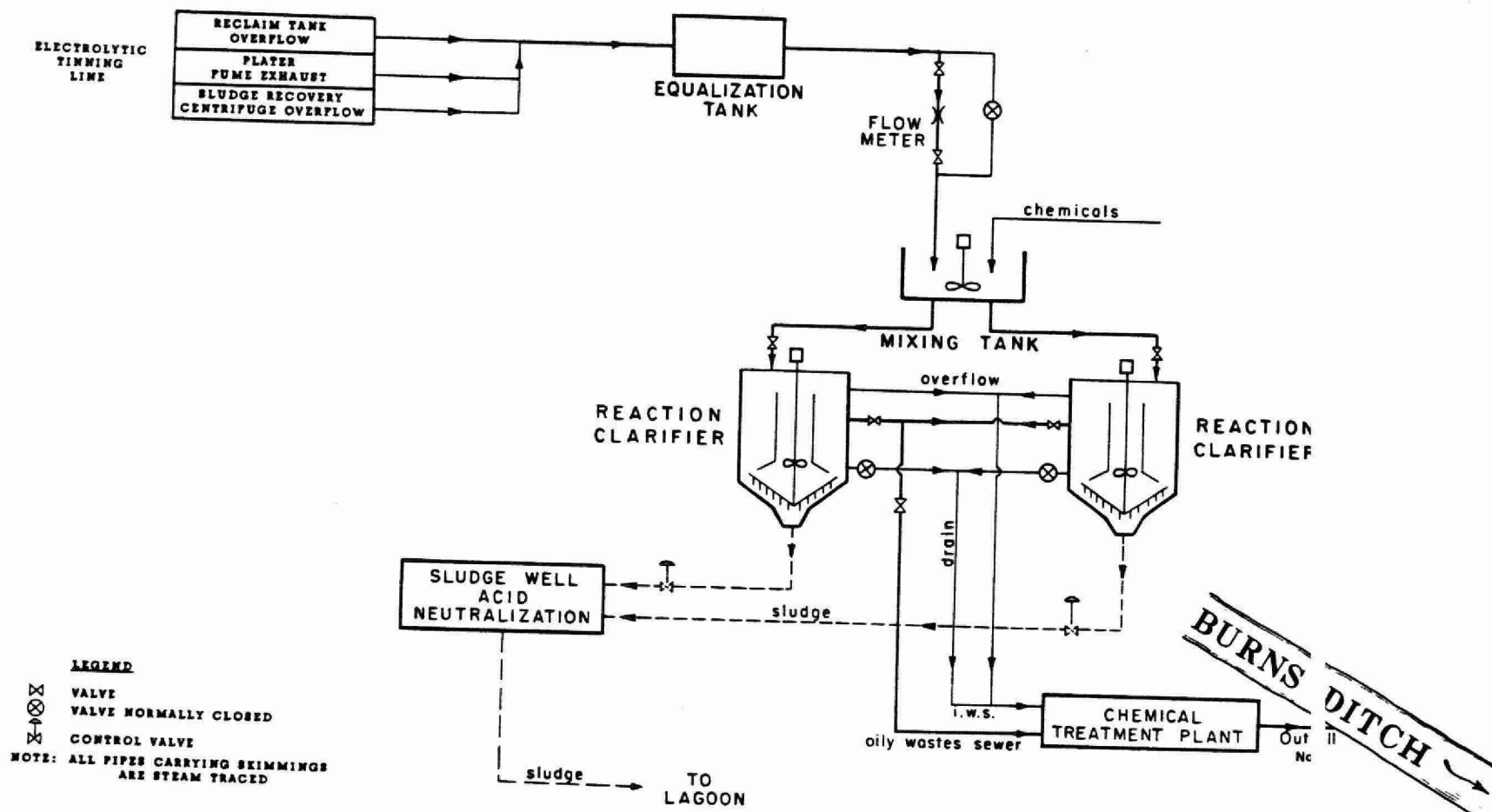


Figure 13A

Finally, only by proper monitoring of the final effluents can management be assured that its investment in facilities and good will is not being dissipated and that its objectives are being met.

REFERENCES

<u>FIGURE NUMBER</u>	<u>DESCRIPTION</u>
1	Photo of undeveloped site of finishing mill
2	Photo of completed finishing mill - same as Figure 5
3	Diagram of product flow
4	Diagram of selected wastes treatment sites
5	Photo of wastes treatment sites - same as Figure 2
6	Photo of sewage treatment plant
6A	Schematic flow diagram of sewage treatment plant
7	Photo of chemical treatment plant
7A	Schematic flow diagram of chemical treatment plant
8	Photo of industrial wastes pretreatment facilities
8A	Photo of acid control building
8B	Schematic flow diagram of acid neutralization plant
8C	Photo of acid neutralization facilities
9	Photo of oil interception plant
9A	Schematic flow diagram of oil interception plant
10	Photo of oil separation plant
10A	Schematic flow diagram of oil separation plant
11	Photo of oil concentration plant
11A	Schematic flow diagram of oil concentration plant
12	Photo of chromium wastes treatment plant
12A	Schematic flow diagram of chromium wastes treatment plant
13	Photo of Fluoride wastes treatment plant
13A	Schematic flow diagram of fluoride wastes treatment plant



"PREDICTION OF RINSING PERFORMANCE
(FOR DESIGN PURPOSES)"

by

J. A. TALLMADGE, JR.

ABSTRACT

Contaminants in adhering solutions are removed in metal finishing operations by immersion of the solid and its adhering liquid in rinse tanks. Rinse design has been studied in order to develop methods for minimizing the amount of rinse water wastes requiring treatment.

The work on rinsing at Yale University during the past six years is reviewed. The initial emphasis was on measurement and prediction of rinsing effectiveness. Since the volume of adhering liquid, or dragout, is also required for rinse design, the emphasis more recently has been on measurement and prediction of dragout and the distribution of the adhering liquid films. Using simple systems, some effects of rinse time, solid shape, and fluid properties have also been considered. Suggestions for future work are discussed in relation to the current state of knowledge of rinse design.

INTRODUCTION

Those familiar with industrial pollution problems have recognized that waste problems may be minimized and sometimes eliminated by changes in the industrial process which gives rise to the waste.

This waste reduction approach has been applied (4, 9) to the washing or rinsing processes, used after such metal finishing operations as plating, anodizing, bright dipping. Several years ago, however, it was realized (5, 9) that the existing design procedures for rinsing operations were limited to those based on an oversimplified assumption, that of complete mixing in the rinse tank.

The work at Yale has been primarily concerned with fundamental studies of the nature and mechanism of rinsing and of the parameters which influence the effectiveness of this washing operation. This work can best be introduced by defining rinsing effectiveness and considering a simple case of rinsing.

(A) Rinsing Effectiveness

Consider the washing of an adhering liquid film on a single object by immersion into a rinse tank. See Figure 1. Let the volume of the liquid film just before immersion be called carryover. After a period of time, the object is removed, carrying with it a volume of adhering liquid called dragout. The bath to which carryover and dragout are referred must be specified to avoid ambiguity, since the carryover for one bath is related to the dragout for the preceding bath. In Figure 1, for example, the carryover to the rinse tank is equal to the dragout from the plating bath minus any drippage during transfer. In this paper, carryover and dragout always refer to the rinse tank unless stated otherwise.

Even where no drippage occurs in transfer, carryover and dragout volumes are generally different. This difference in volume is due primarily to the usual difference in fluid properties between the rinse tank liquid and the liquid in the preceding bath.

The purpose of rinsing is to remove as much of the contaminant in carryover as possible. In other words, it is desirable to reduce to a low value the mass ratio of dragout contaminant to carryover.

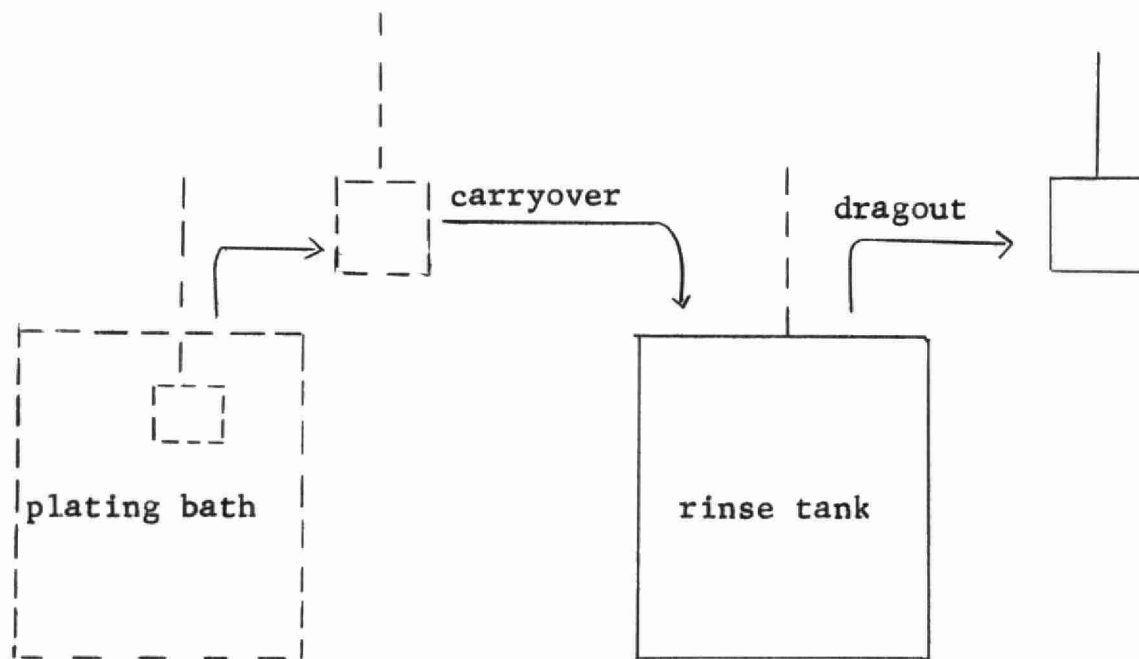


Figure 1. Rinsing of a Single Object

contaminant. Rinsing effectiveness has been characterized by this ratio, which is called U, the unremoved contaminant fraction (5). Thus U is defined as:

$$U = M_D / M_C \quad (1A)$$

where M_D is mass of contaminant in dragout and M_C is mass of contaminant in carryover. Since mass equals the product of concentration and volume, this definition may be written in two other forms:

$$U = M_D / PC_P \quad (1B)$$

$$U = DC_D / PC_P \quad (1C)$$

where D is dragout volume, P is carryover volume, C_D is contaminant concentration in dragout, and C_P is contaminant concentration in carryover.

(B) Some Empirical Measurements on a Flat Plate

To obtain an idea of the size of these quantities, some experiments were performed. Consider the case where a flat plate is immersed vertically in a still rinse under conditions such that dragout and carryover are equal. These conditions were achieved experimentally by dipping and rinsing the plate in baths having water-like viscosity and density and at withdraw speeds such that no carryover drippage occurred.

The dragout volume was measured and found to be 0.88 ml. Then values of U were obtained from independent measurement of contaminant mass in dragout, using equation 1B. Typical values of U are shown in Table 1 along with some of the test conditions. If good rinsing is that where U is less than 1%, then good rinsing was achieved only after several minutes at these conditions.

TABLE 1

Flat Plate Rinse Effectiveness (6)

Rinse Time, seconds	14	107	1007
U, in %	14.2	4.5	1.1

Conditions:

1. Carryover and dragout volumes
 $D = P = 0.88 \text{ ml}$
2. Carryover and dragout density,
 $\rho = 1.00 \text{ gm/ml}$
3. Withdrawal speed, $u_0 = 3.9 \text{ ft/min}$
4. Still rinse of distilled water
5. Size of thin flat plate - about
5 inches square

(C) Design

The definition of U, in the form of equation 1, is useful for reporting known experimental values or rinsing effectiveness as the value U; that is, this form is useful only where the contaminant masses in equation 1A are known, such as by empirical measurement. For design, however, the form which is most useful is the following rearrangement of equation 1C:

$$C_D = UPC_P/D \quad (2)$$

In design, an estimate of dragout concentration, C_D is required. Since carryover concentration, C_D , is usually specified, equation 2 shows that estimates of D, P, and U are required to calculate C_D . As very few equations for estimating these parameters under a variety of conditions were available six years ago, there was a need for developing good design equations for D, P, and U. Since carryover is a function of factors influencing drippage and dragout and U is a function of D, P, and distribution of film thickness, the four essential parameters are:

1. Dragout volume, D
2. Film distribution
3. Drippage
4. Rinsing Effectiveness, U

(D) Rinse Studies at Yale

The primary purpose of this work at Yale is the development of better design equations, both for parameters and for systems. The major emphasis has been on fundamental parameter studies to determine the factors affecting U and, more recently, the factors affecting dragout. Some work has been done on film distribution, but none, to date, on drippage. System design equations for both dragout and tank concentrations for some other rinse systems, such as repeated cycle still rinses and running rinses, were reported in 1961 (5). The factors affecting parameter design equations are discussed in terms of geometrical shapes studied.

FLAT PLATE STUDIES

(A) Rinsing

The only design basis for rinsing performance several years ago was complete mixing, as described in a well written review (4), but predictions from this model give low values of U. For example the U predicted for conditions of Table 1 is about 0.04%. Furthermore, U values predicted from this model are not functions of rate factors, such as rinse time.

The first expression for U developed in this work was based on one of two important mechanisms observed visually, dispersion by molecular diffusion of the contaminant (6). Derived assuming that both carryover and dragout have the fluid properties of water, which implies negligible natural convection and equal carryover and dragout volume, this expression is:

$$U = P/A (\pi D_{AB} t)^{1/2} \quad (3)$$

where P is carryover volume, A is surface area, D_{AB} is binary diffusivity of mass, t is time, and π is 3.14159.

Equation 3 predicts the influence of time and diffusivity quite well for the conditions studied (6). However, the magnitude of U values predicted were about 40% higher than experimental values.

Modification of equation 3 to include the effect of the other important mechanism, drop dispersal, improves the agreement in magnitude with experiment. Such modification, however, requires knowledge of film distribution in carryover and our knowledge in this area is incomplete. Some very recent work of Li (3) on the precise measurements of the bottom drop fraction in carryover indicates that U values may be predictable within 20 or even 10% by this modification.

Two other factors influencing rinsing are the effect of a high density contaminant solution and the effect of flow rate in a running rinse. With the running rinse, we found to our surprise, that there

was very little reduction in U values with rinse flow rates as high as 10 to 20% of the rinse tank volume per minute. Since this was found to be a secondary effect, no prediction or further measurements have been attempted.

Experimental studies of the effect of high density solutions indicate a substantial reduction in U values for densities of 1.04 (7) and 1.4 (1); at 34 seconds, for example, the reduction was from 7% for $P = 1.00$ to about 1 or 2% for higher densities. The U values are, nevertheless, appreciably higher than that predicted from the complete mixing model (about 0.04%). This effect of density is due mainly to natural convection transport in the rinse tank, but is also influenced by differences between carryover and dragout which occur. The next step in this study should be theoretical studies to derive predictive design equations. We would like to continue along this path, but do not currently have anyone working on this program. Other aspects which deserve attention are studies of ways of improving rinsing, but we have not yet been able to begin work in this area.

(B) Reasons for Studying Dragout Volume

Regardless of one's knowledge of factors influencing U, equation 2 indicates that one could not predict dragout concentrations without estimates of dragout volume, D. While this is a sufficient reason for developing methods for predicting of dragout, there are other reasons. In many cases, prediction of carryover and U require understanding of the same factors which influence dragout. Estimates of carryover for rinsing require knowledge of dragout with respect to the previous bath, plus other fluid dynamic effects, such as drippage and drainage - or film distribution. Thus, dragout characteristics are basic to predicting carryover volumes. Furthermore, the distribution of the adhering film is known to influence U values, so that dragout indirectly affects U.

Dragout drainage and drippage problems all are essentially problems in transient fluid dynamics.

(C) Dragout on Flat Plates

Empirical studies mentioned in a review (9) indicated that dragout volumes were proportional to the $1/2$ to $2/3$ power of liquid viscosity and of withdrawal speed. These relationships are not sufficient for design because no basis was provided for determining regions of applicability. This aspect of the problem was resolved by Van Rossum's (8) suggestion that, for negligible end effects, the dimensionless effective film thickness upon dragout, \bar{T} , is a function only of the dimensionless withdrawal speed, which is also called the Capillary number Ca . The definitions of \bar{T} and Ca are:

$$\bar{T} = \bar{h}(\rho g / u_0 \mu)^{1/2}$$

and

$$Ca = u_0 \mu / \sigma$$

where \bar{h} is effective film thickness or dragout volume per total area, ρ is fluid density, g is gravitational acceleration, u_0 is withdrawal speed, μ is liquid viscosity, and σ is gas-liquid surface tension.

Van Rossum showed that these dimensionless groups drew the data into a single, but non-linear, curve, which he represented by a four constant equation implicit in \bar{T} . As the \bar{T} implicit form is not convenient for design, his equation has been approximated in this work, within 2%, by a simpler form. This form, over the range studied, $10^{-4} < Ca < 10$, is:

$$\frac{1}{\bar{T}} = 1.50 + \frac{0.30}{Ca^{0.27}} \quad (4)$$

Using only theory, we have recently been able to predict the $\bar{T} - Ca$ function over the entire 10^{-4} to 10 range of Ca (10). Developed by extending some Russian work, this theoretical but approximate solution agrees with equation 4 within a few per cent.

For low values of Ca from 10^{-4} to 10^{-2} , which is the usual range for aqueous solutions, equation 4 may be approximated, within 1%, by:

$$\bar{T} = 0.80 Ca^{0.15}, \quad (5A)$$

which may be written out as:

$$\left(\bar{h} \frac{\rho g}{u_o \mu} \right)^{1/2} = 0.80 \left(\frac{u_o \mu}{\sigma} \right)^{0.15} \quad (5B)$$

Equation 5 indicates the effect of speed and fluid properties on effective film thickness or dragout volume.

The question of the effect of plate length (or end effects) has not, however, been resolved. Work reported by VanRossum indicates that the end effects due to short plates are measureable, but do not affect dragout volume estimates by more than a few per cent. On the other hand, for the Table 1 conditions at which a dragout of 0.88 ml was measured (6), estimates from equation 4 or 5 were only about 40% of this value. Further work on end effects is planned.

(D) Film Distribution

During transfer from bath to rinse tank, much of the carryover drains to the bottom of the plate so that the film distribution is not uniform. The resultant bottom drop, which may be from 30 to 60% of the total carryover (3), is apparently not rinsed by molecular diffusion. It is removed by dispersal as soon as it touches the surface of the rinse liquid. Our recent experimental studies are not sufficiently general to be of use for design, but do provide important exploratory data. Both experimental and theoretical studies of drainage are needed to develop design equations for predicting distribution.

(E) Summary

Experimental results have been reported for several conditions, but many are not directly useful for

design because of the variety of conditions which occur in practice. However, these experiments are necessary (a) to indicate important mechanisms from which the theory may be developed and (b) to provide a check on the theoretical models developed. Because this author feels that design equations to be general, should, and can be, based on theory, most of the experiments are regarded as the first step in the development of design equations.

Considerable progress has been made in understanding the variables influencing the design parameters of dragout, film distribution, carryover, and rinsing. In some cases, approximate analytical relationships have been developed which indicate the effect of fluid properties, time and speed. Drillage has not yet been studied. However, even for the simple geometry of a vertical flat plate, precise design equations are not available for these parameters.

CYLINDERS AND WIRES

(A) Dragout and Film Distribution

It became apparent that not all flow regimes for cylinder dragout films could be characterized by the single parameter of capillary number which was used for flat plates. Another parameter is necessary. The best one found to date is one which we call Goucher number; where Go equals to ratio of cylinder radius (R) to a function of fluid properties called capillary length, or

$$Go = R / \sqrt{2\sigma/\rho g}$$

Using empirical tests, Van Rossum (8) found that equation 4 was applicable for large cylinders ($Go > 2$), but Goucher and Ward (2) developed a considerably different function for small wires ($Go < 0.04$). Our main effort has been directed toward development of a relationship general for all Goucher numbers. We have done both experimental and theoretical work, but have only preliminary results at this time.

Film distribution studies have been made in preparation for rinse tests, using a high Goucher number cylinder having a 3 cm diameter and 11 cm length. It was found that about 30 to 40% of the dragout sat in a pool on the top of the cylinder (1). Prediction of this top drop portion of dragout involves other theories than those for adhering side films, which are considered in general Goucher number work mentioned above.

(B) Rinsing

Empirical still rinse measurements have been made on this cylinder at two carryover densities and at three rinse times (1). The U values obtained were similar in magnitude to those for a flat plate and the effects of time and density on rinsing effectiveness were also similar to flat plate effects. No theoretical study has been attempted. Theoretical development should probably await a better understanding of the fluid dynamics of cylinder films and flat plate rinsing, both of which are currently under study.

OTHER SHAPES

Some empirical measurements have been made using shapes whose horizontal cross-section is not constant with height. A cube, a sphere, and a funnel were chosen; they have simple geometries for ease in future theoretical developments. The pockets or stagnant areas which catch and hold varying amounts of liquid during dragout, carryover, and rinsing were clearly and quantitatively indicated by preliminary dragout and film distribution results. As expected, the average dragout volume per unit area was generally higher for these shapes than for flat plates; the cube dragout was especially high.

In rinse tests on these objects with water-like carryover solutions (1), the effect of time on U was found to be different than for flat plates. The magnitude of rinsing effectiveness varied considerably; compared with flat plate values, the U values were

lower (funnel) similar (sphere), or higher (cube) depending on the shape. The cube results were of particular interest because of high U values, such as 20% at 100 seconds rinse time. High density carryover solutions, $\rho = 1.40$ gm/ml, have also been rinsed in empirical tests.

It is clear that rinse mechanisms which were not present in plates are important for these shapes and that description of such mechanisms must include the effect of different film distribution and object geometry. No theoretical developments, however, have been attempted. We feel, however, that design equations can and should be derived from theory for these shapes. Better understanding and description of design problems in simpler shapes, if done first however, will probably aid and even expedite theoretical developments for other shapes.

DISCUSSION

(A) Current Status

The objectives of this program are (a) to develop better design equations for the parameters of dragout, drainage, drippage, and rinsing effectiveness as a function of time, carryover density, shape and other factors, (b) to develop better design equations for multi-stage or multi-cycle (complex) systems, utilizing parameter estimates, and (c) to develop ways of improving rinsing.

Neither the problem of predicting performance in a still rinse nor the problem of predicting response of complex systems has been solved. Nevertheless, better estimates are now available and others are being developed.

The work on dragout is also important in other industrial applications, such as in the photographic and coating industries.

(B) Three Countercurrent Rinses

The importance of better estimates of rinsing effectiveness, or U values, is most dramatic in multi-stage systems where the unremoved fraction is a power of the U values. Consider, for example, that three countercurrent rinses are used in series under conditions such that actual U values are 10 times as large as that predicted by complete mixing models, U^* (i.e. $U = 0.5\%$ versus $U^* = 0.05\%$). In this case, final contaminant concentrations on the work would be approximately 1000 times as large as estimated from system design equations based on complete mixing models. Furthermore, actual U values frequently are greater than 10 times the U^* predictions.

(C) Improving Rinsing

While no data has been obtained on the effect of agitation on U , it is interesting to use existing theory to discuss agitation methods. Consider a case where molecular diffusion from the adhering film to the rinse tank is controlling, such as in a flat plate with water-like carryover. It seems that recirculating rinse water would not be an effective method for reducing U as only the bulk liquid would be moved, and its velocity would probably be low. Air bubbling might be better, but this is also primarily a bulk liquid effect. Since some motion imparted to the film or the solid might affect diffusion considerably more, it is suggested that mechanical vibration of the solid be tried. Another related method would be the use of ultrasonics. Shake, rattle, and roll - yes; but concentrate on the film or the solid instead of the bulk of liquid in the rinse tank.

One method of obtaining better rinsing is to consider the effect of time on dragout and drainage. For example, Kushner, in his clear qualitative analysis, concludes that where a specified time for both dragout and drainage is available, a designer should utilize as

much of the time as possible to reduce withdrawal speed. As analytical design equations for estimating the magnitude of these parameters become available, such procedures can be handled quantitatively; optimization techniques could be used if desired.

(D) The Removed Fraction (1-U)

Those interested in waste treatment may ask why this paper is concerned primarily with the concentration in the rinse dragout when the waste treatment design depends only on concentrations in the rinse tank; especially as 1-U values may frequently be approximated by unity for waste calculations. The answer to this is that rinsing is an in-plant process; while good rinse design should consider waste treatment, the primary purpose of rinsing is the manufacture of acceptable products.

(E) Summary

There is considerably more work necessary to place rinse design on a quantitative basis.

ACKNOWLEDGEMENT

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"VEGETABLE CANNERY LIQUID WASTE TREATMENT
BY THE "EVER-FULL" LAGOON SYSTEM"

by

G. DICKSON

INTRODUCTION

The use of lagoons, or stabilization basins, for the purification of liquid wastes has been used by a large segment of the North American Canning Industry for more than a quarter of a century. The subject is well documented in the literature. Perhaps the best known works on the subject is National Canners Association Bulletin No. 26L, "Cannery Waste Disposal Lagoons", by Mr. L. F. Warrick and Mr. T. F. Wisniewski of the Wisconsin State Board of Health, and the late Mr. N. H. Sanborn of the National Canners Association.

It is not my purpose to review the literature on the subject of Liquid Cannery Waste Disposal Lagoons, but instead I will give a report on the current status of lagoons, or stabilization basins, in the Midwest Division of the California Packing Corporation.

THE LIQUID WASTE TREATMENT PROBLEM

The Midwest Division of the California Packing Corporation currently is made up of nine vegetable canning plants located in four states: There are four plants in Illinois, two in Wisconsin, two in Minnesota and one in Indiana. The Divisional Operating Headquarters is at Rochelle, in Northern Illinois.

All the plants are medium to large plants. The products packed are: peas, corn, tomatoes and their products, lima beans, pumpkin, sauerkraut, green and wax beans, and some combination vegetable packs. Peas, corn, green and wax beans, and tomatoes and their products are the largest quantity items.

The liquid wastes of the nine plants are treated as follows:

One plant discharges its waste to the municipal sewage treatment plant. This is tomato waste.

Two plants use spray irrigation.

Six plants are served by lagoon systems.

Geographically the plants served by the lagoon systems are located as follows:

Three in Illinois, two plants using one facility.

One in Wisconsin and two in Minnesota.

All five of the lagoon installations have been in operation for a number of years, although all of them have been modified or enlarged from time to time. The enlargements have been necessary to accommodate additional loading caused by increased production.

The proper preparation of vegetables for canning necessitates the use of large quantities of water. It is safe to say that, for each case of one pound cans packed, 30 to 50 gallons of water has been used to wash and transport the product through the plant. As a result of this use, the water becomes the carrier of considerable quantities of vegetable nutrients that will render it susceptible to bacterial attack. The quantities, just mentioned, do not include the water used as a packing medium or water used to cool the cans after they have been processed.

Cooling water, devoid of organic pollution, is segregated to be disposed of without treatment except by cooling and re-oxygenation.

WHY LAGOONS?

The question naturally arises, "Under what circumstances does a lagoon system become the treatment method of choice?" The answer to this question is sometimes very complex, but on the whole it is safe to say that, in most cases, lagoons are used when there is no other practical way of doing the job.

Vegetable canneries, for the most part, are located in small towns and, in some cases, in strictly rural areas, with the idea of reducing the transportation cost of the raw product and keeping the time factor between harvest and packing to a minimum. The cannery is located as close as possible to the source of raw product supply.

The liquid waste from the canneries located in some small towns may be 30 or 40 times that of all the domestic waste originating with the population. Our plant at Arlington, Wisconsin, illustrates this situation quite clearly. The village has a population of 350 people. The sewage plant is geared to the population. The liquid waste from the cannery will accumulate a waste water volume of 60 million U. S. gallons with a pollution load of 400,000 pounds of BOD per season.

Irrigation, either spray or row, has produced satisfactory results; but irrigation is limited in its application to locations where suitable land can be obtained within a reasonable distance of the plant.

If there is no available city sewage plant with capacity to handle the cannery wastes, and land cannot be found that will accommodate itself to spray or row-irrigation, the only alternative that is left is to treat the cannery wastes by the lagooning method.

HOW WASTE TREATMENT LAGOONS ARE OPERATED

Cannery lagoons, when considered in the conventional way, are classified as either (1) absorption or (2) storage.

Absorption Lagoons can be and are used in locations where soil is porous, a rapid absorption rate can be maintained, and there is no peril of polluting the underground water supply or a nearby stream. I have personal knowledge of both these things happening. Where absorption lagoons were used, it may be well to mention, at this point, that the two hazards just mentioned also apply to any type of a waste irrigation system.

Storage Lagoons are far more common than the absorption type, and when operated in the conventional manner, are of sufficient capacity to impound the liquid waste from the plant being served for an entire canning season. They are sometimes constructed as a single unit and often multiple units are employed.

The material going into the lagoon is usually screened to remove as much of the solids content as possible. A 20 to 40 mesh screen is usually employed. If properly operated, good equipment provided with the proper screens will remove all but the finely divided suspended solids.

The water is thus impounded until the soluble and suspended solids have been broken down by microbial action to end products that are no longer capable of causing odours or polluting receiving waters.

Storage lagoons are usually drained the spring following collection, if possible, during the high water season. In some states, draining can be done only with the permission of some state agency, but in all cases the canner is liable for any damage to aquatic life or the degradation of riparian rights along the receiving stream or lake.

SOME OF THE PROBLEMS

Odour in connection with cannery lagoons, has often been a serious problem. Warrick, Wisniewski, and Sanborn found that when lagoon depths between 3 and 5 feet were maintained, fairly effective odour control could be realized in most cases, if sodium nitrate was added in sufficient quantity to keep the bacterial population on the aerobic side. As a matter of practical application, the depths of lagoons were very seldom held to the 5 foot maximum depths recommendation, and the regular dosage of sodium nitrate at an effective rate was not provided.

The maintenance of dikes is always a problem. Rodents and wave action are constant and unrelenting enemies of the lagoon keeper, as are noxious weeds of a hundred varieties. Under certain circumstances, mosquito breeding is at an optimum.

Because of the various nuisances attending lagoon treatment of wastes, this method has been somewhat in disrepute of late, but, because no other practical method was available, has been tolerated, like the town dog catchers.

A NEW APPROACH TO THE LAGOONING PROBLEM

Several years ago, we became interested in reports by the U. S. Public Health Service and others, dealing with the use of stabilization ponds to treat domestic sewage in the North Central States. According to these reports, domestic wastes had been successfully treated using 2 or 3 stage lagoons, maintained on an "ever-full" basis, discharging an acceptable effluent to a public water way. We postulated that vegetable cannery wastes could be successfully treated in the same way.

All of our lagoon systems are constructed in multiple units. This type of construction was mainly due to production expansion. When additional lagoon space was needed, it was found to be easier and more

practical to add an additional pond than enlarge an existing one. Most of these systems could be altered to hook a number of ponds in series.

We selected the Sleepy Eye, Minnesota installation for our initial venture into the Continuous Ever-Full Lagooning operation.

The Sleepy Eye plant is located in the South Central part of Minnesota. At this plant we pack peas, Whole Kernel corn, and Cream Style corn. The plant, on an average year, will have a waste water output of approximately 60,000,000 U. S. gallons that carries a pollution load of approximately 500,000 pounds of BOD.

The waste water is discharged into the lagoon system over a period of 90 days.

The lagoon System, 38 acres in all, was modified to provide for a series flow progressively through six large ponds and a small one before being discharged into an adjacent drainage canal, which, in turn, feeds into a rather small river about 4 miles distant. Each pond was connected with the next one in the series by an 18-inch tube, equipped with a slide type headgate, so that each unit could be isolated if the need should arise. By altering the setting of the headgates, depths of anywhere from 3 to 5 feet could be produced.

In the spring of 1961, after the bottoms of the ponds had been leveled to eliminate both deep and shallow areas, and the dikes repaired, waste water was discharged into the system. Until sufficient excess water had accumulated in one pond to completely cover the bottom of the next unit, the gate between the two was kept closed. Until water was let into a unit weed growth was prevented by repeated cultivations.

Sodium nitrate was added to the ingoing waste at the rate recommended in N.C.A. Bulletin 26L.

At the completion of the operating season, all units of the system were full. At this point we

installed a gasoline driven pump on the bank, between the first and the sixth unit, and the waste water was pumped back to unit #1. This pumping was continued until the water in all units had equalized from a BOD standpoint.

After the re-circulation process had been completed on November 6, the 5-day BOD value in the six units was approximately 400 ppm. By the time ice started to form on the ponds, December 1, the BOD values had dropped to 300 ppm. All units were carrying a heavy algae growth at the time of the freeze over.

There was no detectable odour coming from any of the ponds when the re-circulation had been completed.

The ice broke up early in April and we resumed our BOD testing schedule. Within a week after the break-up, the 5-day BOD values in all the ponds averaged 50 ppm. Algae growth began when the ice disappeared, and all ponds carried heavy populations of algae, mostly of the single-cell green types.

By the time the pea operations began June 18, for all intents and purposes, the water in the system was completely stabilized.

During the winter and spring, the water loss through seepage and evaporation had lowered the water level approximately 18 inches below the high water mark of the previous fall.

The pea operation started on June 18 and continued until August 5. During this time there were 42 operating days, producing approximately 30 million gallons of waste water carrying a pollution load of approximately 150,000 pounds of BOD.

It took about 10 million gallons of waste water added to pond #1 to bring the level of all units up to the point where water was discharging from the last unit into the receiving stream. During the pea

season, approximately 20 million gallons of water were discharged from the lagoon system into the receiving stream.

Table #1 summarizes the 5-day BOD and pH values of samples taken at weekly intervals from each of the 7 units.

During the period covered by Table #1, no sodium nitrate or any other chemical was used for odour control. Observations made by people, acquainted with our lagoon system for years confirmed our opinion that the odour produced during the pea season was much less than normal. For the first time in several seasons there were no complaints from the public.

The plant was idle for two weeks between pea and corn packs. Starting August 19, continuing through September, and for more than a week into October another 30 million gallons of waste water was discharged into the system, carrying a polluttional load of very close to 300,000 pounds of BOD from corn waste. Although the same in volume as the pea waste, it carried double the polluttional load.

Table #2 summarizes the BOD and pH value for each pond during the corn canning season.

By the first week in September the algae in the last two units began to disappear. The water became clear enough so that the bottom of the ponds became visible; at the same time many aquatic insects and fresh water snails became established in these ponds.

During the entire period that we were discharging treated waste water, we monitored the receiving waters for dissolved oxygen and made frequent inspection trips along the waterway looking for signs of even marginal pollution. The dissolved oxygen of the receiving waters was always near or at the saturation point, and no signs of any damage to the stream could be found at any time.

TABLE # 1 - PEAS - 1962

<u>DATE</u>	<u>UNIT #1</u>		<u>UNIT #2</u>		<u>UNIT #3</u>		<u>UNIT #4</u>		<u>UNIT #5</u>		<u>UNIT #6</u>		<u>UNIT #7</u>	
	<u>5-Day</u> <u>BOD</u>	<u>pH</u>	<u>5-Day</u> <u>BOD</u>	<u>pH</u>	<u>5-Day</u> <u>BOD</u>	<u>pH</u>	<u>5-Day</u> <u>BOD</u>	<u>pH</u>	<u>5-Day</u> <u>BOD</u>	<u>pH</u>	<u>5-Day</u> <u>BOD</u>	<u>pH</u>	<u>5-Day</u> <u>BOD</u>	<u>pH</u>
6-18	14		13		18		15		15		15		13	
7-3	488		62		21		32		16		17		16	
7-23*	694	6.6	386	7.3	150	7.5	27	7.9	41	7.7	57	7.6	37	7.6
8-1*	486	6.9	231	7.6	51	8.1	37	8.2	32	8.1	29	8.1	26	8.0
8-7	337	7.2	190	7.3	58	7.6	23	8.0	19	7.89	17	7.8	17	7.7

*NOTE: Heavy Wind - bringing up sludge from the bottom.

TABLE #2 - CORN SEASON - 1962

DATE	UNIT #1		UNIT #2		UNIT #3		UNIT #4		UNIT #5		UNIT #6		UNIT #7	
	5-Day BOD	pH	5-Day BOD	pH	5-Day BOD	pH	5-Day BOD	pH	5-Day BOD	pH	5-Day BOD	pH	5-Day BOD	pH
8-7	337	7.2	190	7.3	58	7.6	23	8.0	19	7.8	17	7.8	17	7.7
8-23	498	6.6	86	7.4	47	7.7	24	7.7	23	7.7	21	7.7	19	7.7
8-27	1324	6.4	241	7.3	90	7.6	65	7.7	31	7.8	20	7.7	14	7.7
8-31	774	6.3	294	7.2	66	7.8	22	7.8	19	7.8	15	7.7	16	7.7
9-4	1433	5.3	563	6.9	152	7.3	70	7.5	34	7.6	15	7.5	14	7.5
9-10	1523	6.2	848	6.8	173	7.3	51	7.4	40	7.5	13	7.5	12	7.5
9-13	2153	5.3	1163	6.7	215	7.4	49	7.8	42	8.0	15	7.5	16	7.5
9-17	1987	5.6	922	6.7	172	7.3	52	7.5	39	7.7	13	7.5	12	7.5
9-20	1408	5.9	1003	6.6	293	7.4	60	7.6	41	7.7	14	7.3	15	7.3
9-28	2033	5.5	1418	6.3	601	7.1	92	7.3	59	7.3	18	7.3	11	7.3
10-5	2393	5.6	1493	6.3	678	7.0	228	7.2	104	7.2	41	7.2	13	7.2
10-11	1733	5.7	1353	6.5	833	7.1	257	7.2	83	7.4	45	7.5	14	7.3

During the 1963 canning season, the Sleepy Eye lagoon system was again operated on the "ever-full" basis. Due to crop variations, the BOD loading from peas dropped to 133,000 pounds, and the load from the corn operation increased to 430,000 pounds. The total loading increased to 663,000 pounds of BOD in 1963 as compared to 450,000 pounds in 1962.

Despite this increase in loading, the system continued to produce a satisfactory effluent that caused no damage to the receiving waters, measured by a depression of dissolved oxygen or the creation of a nuisance.

Table #3 summarizes the results of treatment for the 1963 season.

CONCLUSION

After reviewing the results we obtained at Sleepy Eye in 1962, we set up two additional "Ever-Full" lagoon installations in the Midwest Division, one at Rochelle, Illinois, and the other at Mendota, Illinois. As the 1963 season can be regarded as the "start-up" year, we have as yet insufficient data on these installations to warrant more than their mention in this paper. However, I can say that these preliminary data indicate strongly that we can expect results this canning season comparable to those achieved at Sleepy Eye in 1962 and 1963.

Lastly, we have obtained from the State Boards of Health, of both Minnesota and Wisconsin, permission to change the last two "fill and dump" lagoons we have in the Midwest Division over to the "Ever-Full" method of operation. So this canning season we will be started the new system at Wells, Minnesota, and Arlington, Wisconsin.

All these installations deal with the same type of wastes, originating from corn, peas and lima beans. The polluttional load is composed of vegetable sugars, starches and proteins that are very easily

TABLE #3

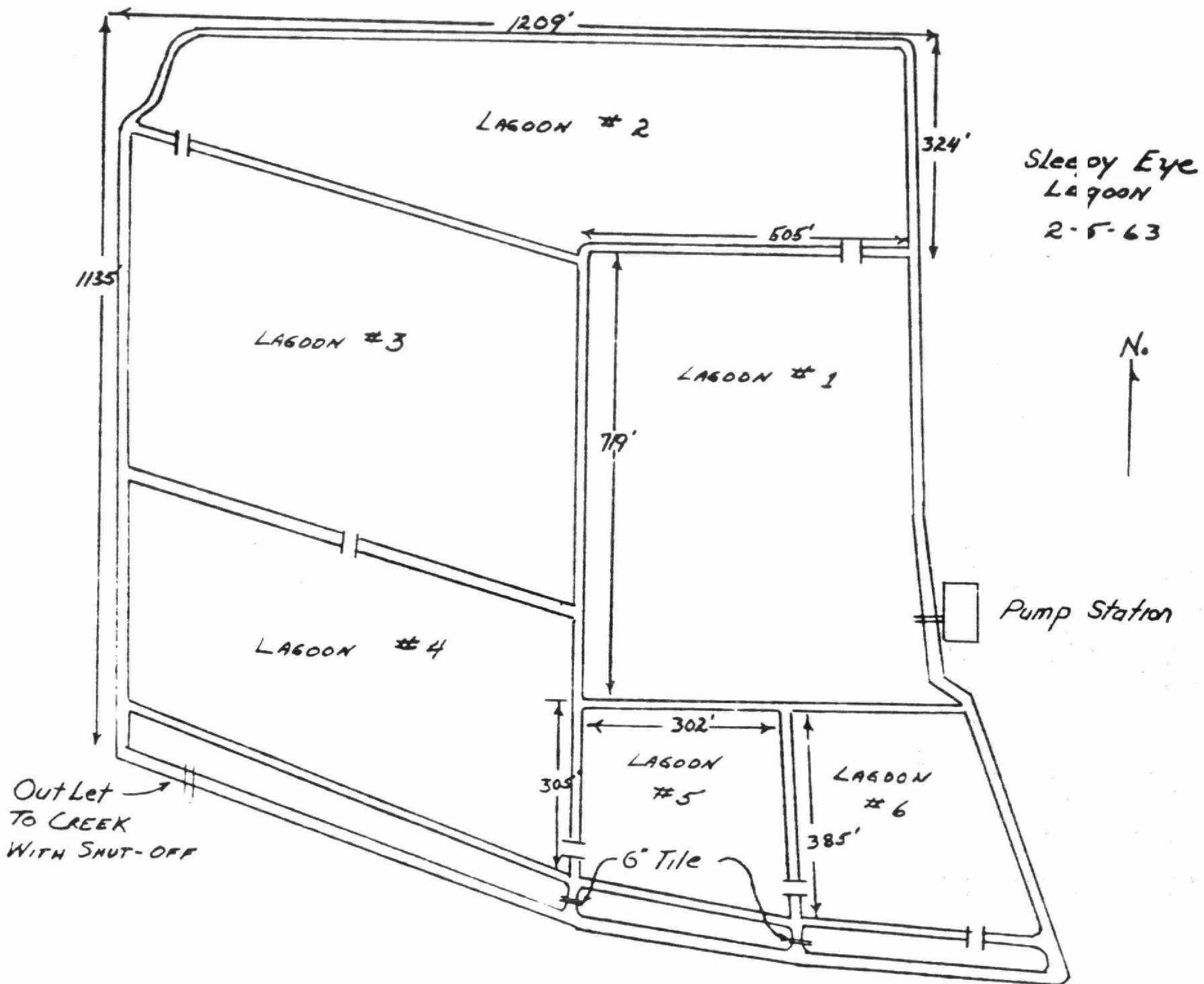
SLEEPY EYE LIQUID WASTE TREATMENT DATA - 1963 SEASON

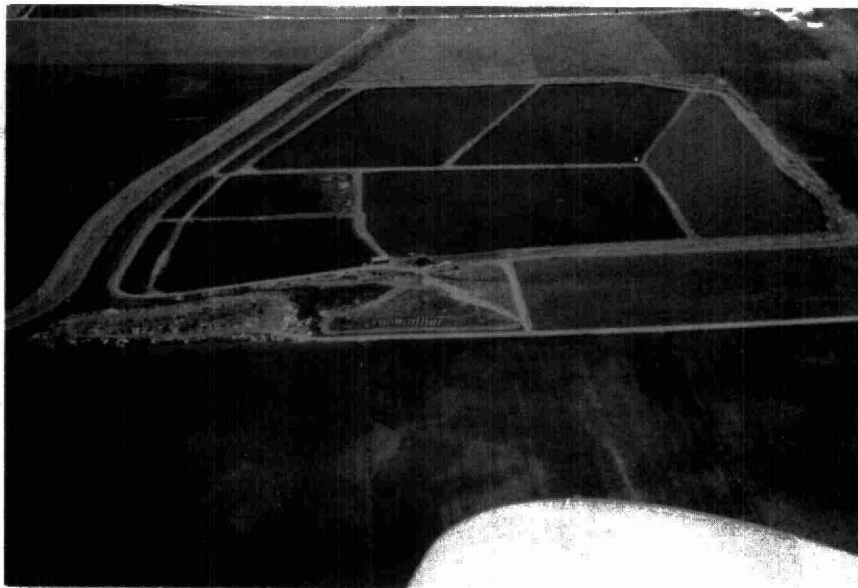
<u>DATE</u>	<u>BASIN #1</u>		<u>BASIN #2</u>		<u>BASIN #3</u>		<u>BASIN #4</u>		<u>BASIN #5</u>		<u>BASIN #6</u>		<u>BASIN #7</u>	
	<u>pH</u>	<u>BOD</u>	<u>pH</u>	<u>BOD</u>	<u>pH</u>	<u>BOD</u>	<u>pH</u>	<u>BOD</u>	<u>pH</u>	<u>BOD</u>	<u>pH</u>	<u>BOD</u>	<u>pH</u>	<u>BOD</u>
6- 1-63	8.2	50	8.4	90	8.5	90+	8.0	18	7.6	90	7.3	16	7.3	12
7-11-63	6.6	580	7.7	126	8.2	64	8.1	57	7.7	24	7.4	22	7.4	24
7-15-63	6.5	720	7.3	198	7.8	49	7.6	47	7.5	15	7.3	16	7.3	15
7-19-63	6.7	690	7.4	312	7.7	90	7.8	65	7.7	17	7.5	19	7.4	17
7-29-63	7.0	600	7.5	340	7.7	85	7.9	60	8.2	14	8.1	21	8.0	37
8-11-63	7.2	490	7.7	305	7.7	75	8.1	62	8.4	42	8.5	29	8.4	22
8-16-63	6.5	610	7.1	190	7.7	85	8.3	88	8.5	68	8.5	39	8.4	31
8-29-63	6.5	660	6.9	435	7.3	95	8.0	71	8.5	39	8.4	29	8.2	19
8-31-63	5.4	1538	6.4	900	7.2	294	7.6	82	8.0	64	8.3	33	8.3	23
9- 6-63	5.9	1200	6.4	1013	7.2	315	7.7	90	8.0	52	8.3	37	8.3	26
9-17-63	6.0	1620	6.3	1320	7.0	540	7.5	138	7.6	48	7.7	34	7.9	21
9-21-63	5.8	1530	6.3	1020	7.0	645	7.5	116	7.6	38	7.9	26	7.9	19

BOD reported in parts per million.

broken down by bacterial action and is a medium in which almost any type of soil borne organism thrives without supplemental feeding. At the present time my personal knowledge and experience covers only this one type of waste.

I would strongly advise all of you that, on the basis of our experience reported here today, you do not go out and build yourself a lagoon system without first considering the type and strength of the wastes you intend to treat, the climate, the soil and a good many other factors, including legal regulation in your locality. Each waste treatment problem is individual, but they all must be solved.





Sleepy Eye Lagoon
July 1

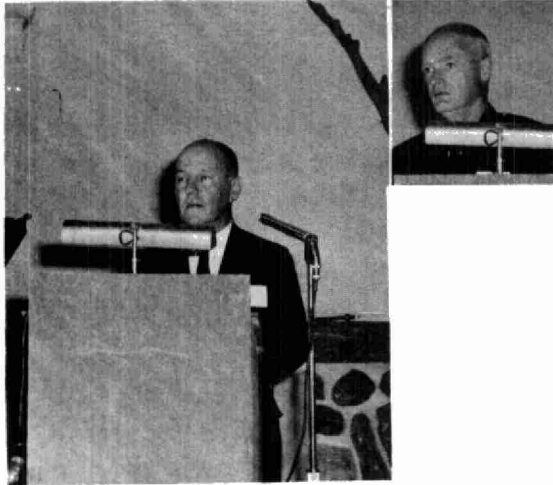


Sleepy Eye Lagoon
Late September



THE BANQUET

SESSION FOUR



C. H. D. Clarke
Ontario Department of Lands & Forests
Fish & Wildlife Branch
Session Chairman

"TESTING AND RATING
SURFACE AERATORS"

by

A. R. SMITH

The testing and rating of surface aerators is a fairly simple thing. The testing procedure has not been standardized, however, so it is sometimes difficult to compare the performance of different units. This paper will outline the use of surface aerators, the testing and rating of aerators, and some of the information that is required before aerators can be compared. Mathematical proofs will be kept to a minimum for the benefit of those who have been out of school these many years.

NATURAL WASTE TREATMENT

Surface aerators are used in waste treatment to simulate the so-called "self-purification" of streams. Sewage dumped into a flowing stream provides food for bacteria living in the water. They convert it into inoffensive substances - water, carbon dioxide, and stable chemical compounds. These bacteria operate much like a human cell. Food and oxygen are required for energy and new cell material and both are absorbed through the cell wall. The source of oxygen is the dissolved oxygen (DO) in the water. As long as there is enough oxygen, the bacteria will thrive.

As the bacteria remove oxygen from the water, it is replenished by absorption of oxygen from the air at the water surface. If the quantities of food, bacteria, and oxygen are in balance, everything works fine. Oxygen is sparingly soluble in water, however, and for every stream there is a limit of how rapidly it can be transferred from air to water. If the amount of sewage dumped in the stream is increased, the bacteria will multiply until their requirements for oxygen exceed the amount transferred from the air. Further dumping of sewage will result in a complete depletion of dissolved oxygen. At this time, different forms of bacteria take over. They use the oxygen bound up in the sewage. These bacteria produce noxious end products - black scum, smelly gases, etc.

The balanced system is called aerobic, the oxygen depleted system is called anaerobic, or septic.

A rapidly running stream, with lots of surface turbulence caused by rocks and other obstructions, will be able to purify more sewage than a placid stream. The water will bubble and spray, constantly exposing new surfaces to the air. More oxygen will be absorbed, more bacteria will thrive, and more sewage can be treated.

The word sewage, as used in this discussion, is meant to include both domestic sewage and those industrial waste waters which can be treated biologically.

BIOLOGICAL WASTE TREATMENT

In biological waste treatment, the bacteria are confined under controlled conditions in a tank or lagoon. Oxygen is transferred to the water by bubbling air through it or by creating surface turbulence, say, with a surface aerator. The strength of the sewage indicates the amount of food available for the bacteria and, roughly, the amount of oxygen the bacteria will require to use the food.

This is not intended as a treatise on sewage treatment but a brief rundown on how sewage strength is determined may be helpful. A small, measured sample of

sewage is added to standard dilution water in a bottle about one pint in capacity. The dissolved oxygen (DO) of the water is determined, and the bottle incubated for 5 days at 20°C. The DO is again determined. The difference in DO from the original is that consumed by bacteria feeding on the waste. The quantity of oxygen consumed is the measure of strength of the sewage. It is expressed in parts per million (ppm) of BIOCHEMICAL OXYGEN DEMAND, or BOD, as it is commonly known. If the flow is known, we can convert ppm into pounds per day or per hour. Ordinary domestic sewage has a BOD of about 200 ppm. Thus, for a daily flow of 100,000 gallons, there are $100,000 \times 8.34 = 834,000$ pounds of sewage, and 0.834 million pounds $\times 200$ ppm, or 167 pounds of BOD. If 90% BOD is removed, the biological load is $167 \times 0.9 = 150$ pounds per day. The degree of treatment percentage of BOD removed can be controlled by changing the number of bacteria under aeration and the aeration period. Anywhere from 1 pound to 1.5 pounds of oxygen are required to treat each pound of domestic sewage BOD removed, depending on the type and efficiency of treatment. Surface aerators are designed to transfer the required oxygen from air to the sewage.

TESTING SURFACE AERATORS

Surface aerators are rated on how many pounds of oxygen they will transfer into water in an hour. The amount of oxygen cannot be measured directly because it does not come from bottles or a compressor. The aerators simply create turbulence, like a rapidly running stream, to expose as much water to the air as possible with the least expenditure of horsepower.

The transfer of oxygen from air to water was originally studied using air bubbles released at the bottom of a tank. The amount of air could be measured as could the size and number of bubbles. The trick is to get the maximum surface contact between air and liquid, for each volume of air. It is at these contact surfaces, or interfacial areas, that the oxygen passes from the air and is dissolved into the water. Many small bubbles obviously are more effective than few

large ones. For example, one cubic foot of air in one bubble has only 4.8 square feet of contact area, but when divided into bubbles of the size commonly produced by air diffusers (1/10 to 1/8 in), one cu. ft. of air has about 700 sq. ft. of contact area. Much of the nomenclature used in oxygen transfer work is a carry-over from these bubble studies.

These studies showed that the transfer of oxygen from air to water is influenced by several factors. These will be discussed one by one.

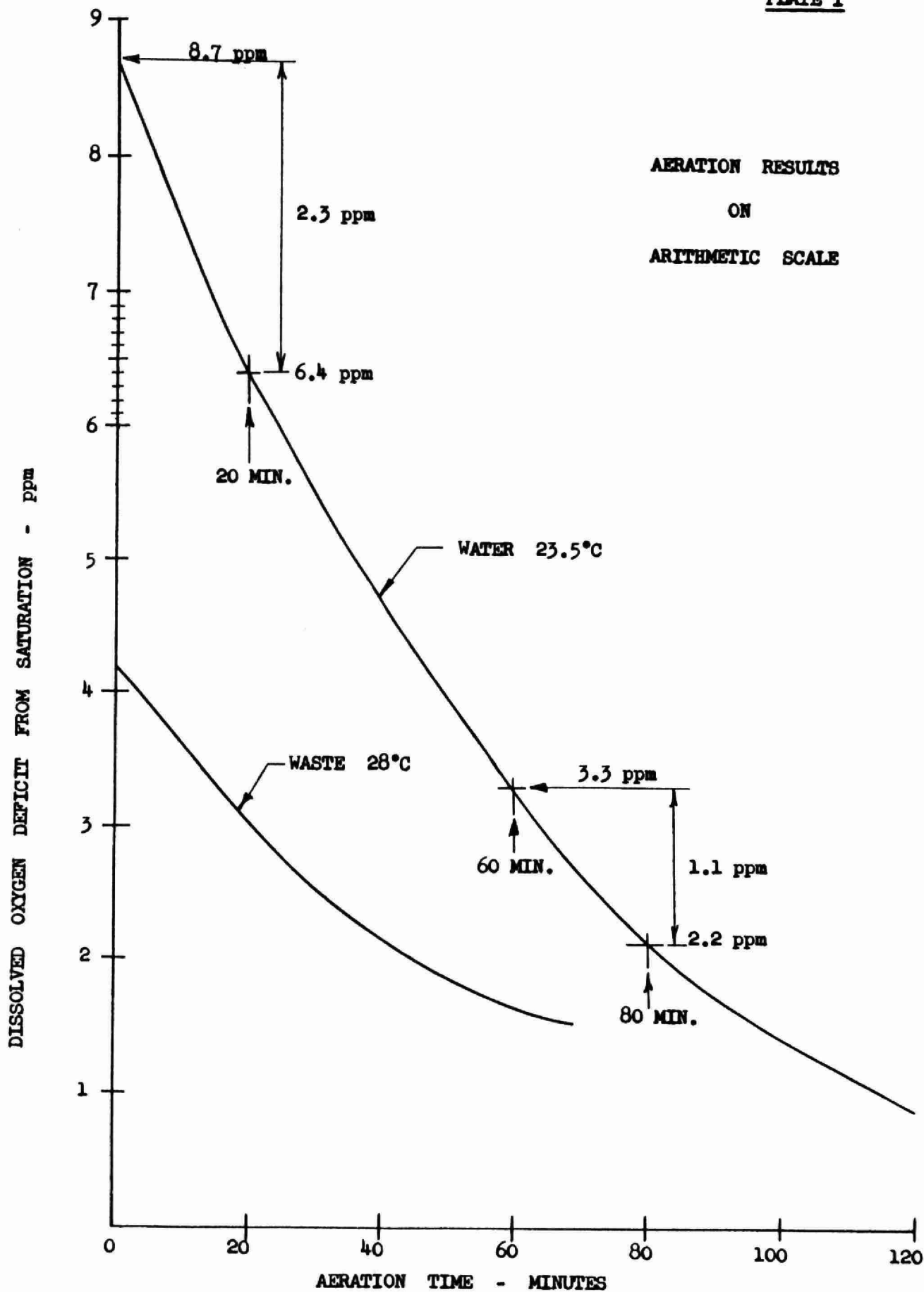
Existing DO Content of the Water

Obviously no oxygen will be transferred if the water is saturated. At the other extreme, it has been found that the greatest rate of transfer occurs when the water is completely devoid of oxygen. Thus, the general rule: The rate of transfer of oxygen from air to liquid varies directly as the under-saturation or oxygen deficit of the liquid. The oxygen deficit is often called the driving force.

This is shown graphically on Plate I. We have plotted the data obtained in two tests. In one, we deoxygenated a tank of pure water by adding an oxygen scavenger, sodium sulphite. Thus, we started with water with zero DO. An aerator was mounted on top and started. As the water was agitated, oxygen was absorbed and the DO began to rise. It was measured and recorded at various intervals of time. The saturation for water is known so we could find the oxygen deficit at the time we took our DO readings.

In Plate I, the oxygen deficit is plotted against time. One curve is for pure water, the other for a waste water. Ignore the latter for the time being. The saturation DO value for the water is 8.7 ppm, as shown on the Plate.

Note that in the first 20 minutes of aeration, the DO deficit has decreased from 8.7 to 6.4 ppm, or 2.3 ppm, and after an hour, the following 20 minute aeration period reduces the deficit from 3.3 to 2.2 ppm, or only 1.1 ppm.



The above test is the basis for comparing surface aerators. In one hour the oxygen deficit has been reduced from 8.7 ppm to 3.3 ppm, or 5.4 ppm. If the tank holds 60,000 gallons, or 500,000 pounds of water, the amount of oxygen transferred is 5.4 pounds/ per million pounds x 1/2 million pounds, or 2.7 pounds per hour. Another surface aerator may transfer more or less oxygen during the same period and if we know the horsepower, we can compare units on the basis of pounds of oxygen transferred per hour per horsepower.

The test just described has been run under non-steady state conditions, in which the DO deficit has changed from maximum to zero. In waste treatment, the aerators are used to replenish the oxygen being used by the bacteria. The oxygen must pass through another interfacial area at the cell wall. The bacteria do not maintain a high level of oxygen concentration within the cell wall, so a minimum DO of 2 ppm in the aeration tank is usually more than adequate to effect the transfer of oxygen through the cell wall.

The conditions under which the aeration system must operate are becoming established. The driving force, or available DO deficit, is limited to the difference between the 2 ppm that must be maintained in the aeration tank and the saturation value of the aeration tank liquid (water plus bacteria plus sewage which is called mixed liquor). This is called the steady state condition because the DO level remains fixed.

The rate of transfer (in ppm per hour) at 2 ppm DO in the aeration tank is represented on Plate I by the slope of the curve where the oxygen deficit is 8.7 - 2.0 or 6.7 ppm. Sound familiar? This, of course, is a basic calculus problem. We can find the rate of transfer at any oxygen deficit if we can determine the slope of the curve at that point.

As stated before, the aeration curve shown on Plate I is for one aerator. A different type aerator will produce a different curve, depending on the relative amount of turbulence created, and thus on the relative rates of oxygen transfer.

We have so far described two things that influence the rate of oxygen transfer. One is the oxygen deficit, which is independent of the aerator, and the other is the characteristics of the aerator which induces the turbulence - shape of blades, height of blades, RPM, etc. The latter would remain constant in a test so they are included in a constant - K_{LA} . There are other things that affect the values of K_{LA} but we will discuss these later. The subscripts are a hold-over from the bubble aeration studies and refer to bubble areas and liquid film coefficients. The subscripts do not apply in surface aerator studies but the term, K_{LA} , is used in most aeration literature so it is used here.

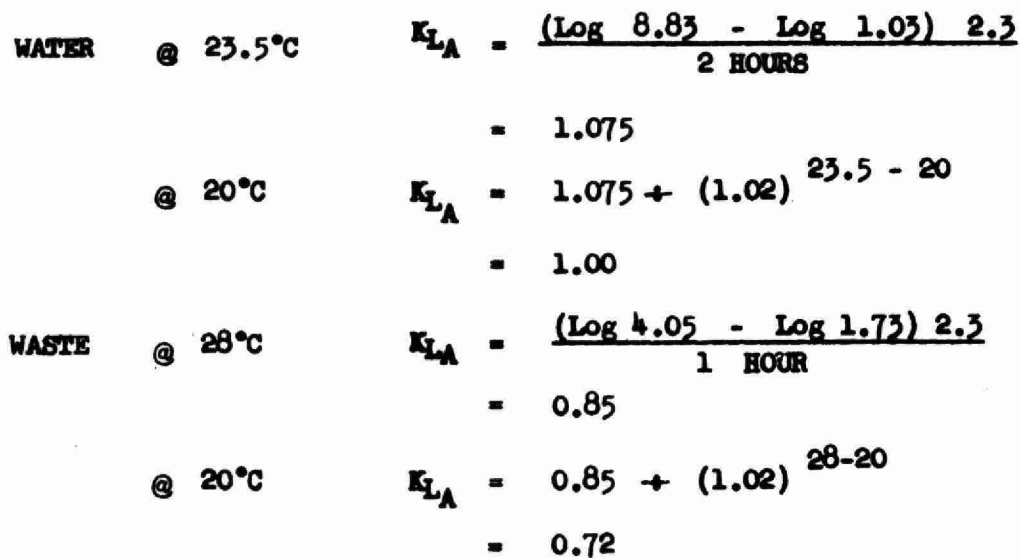
As a general statement, we can say the rate of oxygen transfer, i.e. the change in concentration (c) in time (t), is equal to the oxygen deficit (the saturation concentration C_s , minus the existing concentration (C) times a constant K_{LA} , or

$$\frac{dc}{dt} = K_{LA} \times (C_s - C)$$

This equation can be solved by integration or it can be done graphically, as on Plate II. K_{LA} is the slope of the curve, a straight line in this case, and as we will rate the aerators on oxygen transferred in an hour, K_{LA} is expressed as ppm/hour/ppm concentration deficit. This terminology is rarely used. The constant is usually expressed as K_{LA} per hour, such as $K_{LA} = 3/\text{hr}$. It is called the overall oxygen transfer coefficient.

The solution on Plate II shows the log of the concentration change divided by the time in hours. If the equation had been solved by calculus, the logs would be to the base e. The number 2.3, converts from the base 10, to which the paper is drawn, to the base e.

For the test in water, the K_{LA} is 1.0 hour. The number 1.0 is just a coincidence. The date was obtained from an actual test and it just came out that way.



Returning to Plate I, the slope of the curve is equal to the rate of oxygen transfer in ppm/hour. Now K_{LA} is known, these rates can be determined for any oxygen deficit, in accordance with the equation

$$\frac{dc}{dt} = K_{LA} \times (C_s - C), \text{ where oxygen saturation } C_s = 8.7 \text{ ppm}$$

Assume the test tank holds 30,000 gallons, or 250,000 lbs.

$$\left(\frac{1,000,000}{4} \right)$$

DO, ppm	Oxygen Deficit ppm	K_{LA} /hr	Rate ppm/hr	Lbs. oxygen per hour
0	8.7	1.0	8.7	2.18
1	7.7	1.0	7.7	1.93
2	6.7	1.0	6.7	1.68
3	5.7	1.0	5.7	1.43
etc.				

Effect of Temperature

Temperature has two opposite effects on oxygen transfer.

The saturation value of oxygen in water increases as the temperature decreases. If we maintain 2 ppm DO in the aeration tank, the oxygen deficit increases as it gets colder. Thus, the driving force increases and the rate of transfer increases in proportion.

On the other hand, experiments have shown that at the same oxygen deficit, more oxygen will be transferred to warm than to cold water. This is probably due to a change in viscosity. This variation in oxygen transfer rate is included in the transfer coefficient, K_{LA} . If K_{LA} is determined at some temperature other than the usual standard, 20°C, K_{LA} 20 can be determined by the equation:-

$$K_{LA} = \frac{K_{LA}}{(1.02)^{t-20}} \text{ where } t \text{ is the}$$

temperature at which the test was run. This correction was made on Plate II. The constant 1.02 has been determined experimentally.

Effect of Waste Constituents

The saturation value of a waste may differ from that of pure water. The saturation value of sewage is about 90-95% that of pure water, although the mixed liquor in an aeration tank or lagoon is usually considered that of water, unless the engineer specifies otherwise.

Some chemicals also affect the saturation value. The following table gives the DO value of pure water, and water containing various amounts of chlorides, at different temperatures. DO values are in ppm:-

Temperature		Chlorides, ppm		
C°	F°	0	5,000	10,000
0	32	14.62	13.79	12.97
5	41	12.80	12.09	11.39
10	50	11.33	10.73	10.13
15	59	10.15	9.65	9.14
20	68	9.17	8.73	8.30
25	77	8.38	7.96	7.56
30	86	7.63	7.25	6.86

Other constituents change the oxygen transfer coefficient, K_{LA} . Soap changes the surface tension of the liquid and decreases rate of oxygen transfer. Some paper mill wastes enhance oxygen transfer. More oxygen is transferred to the waste than to water under the same conditions. This characteristic can be found only by testing.

Plates I and II actually show a laboratory test on water and a refinery waste. Two identical beakers and mixers were used. Both samples were deoxygenated, the stirrers were started, and the increase in DO recorded. K_{LA} 's were determined and the K_{LA} at 20 C° computed. Thus, in two identical aeration systems, more oxygen was

transferred to the water than to the waste. The ratio of the K_{LA} of the waste to that of water is called the alpha value (α). If an aerator is rated in pounds of oxygen transferred to water, this figure is multiplied by alpha to obtain the pounds transferred to the wastes, all other conditions being equal.

The alpha value of the waste on Plate II is $\frac{0.72}{1.0}$ or 0.72.

The alpha value commonly used for domestic sewage is 0.8.

A surface aerator may also be tested under actual operating conditions, as follows:-

1. Determine the operating DO content of the mixed liquor, and also the saturation value. Then the oxygen deficit can be calculated.
2. A sample of mixed liquor is agitated until it is saturated with oxygen. It is then stirred gently to keep the solids in suspension, but not hard enough to introduce oxygen from the air. DO readings are taken at intervals to determine the oxygen uptake rate, or oxygen demand, of the system. From this information the total oxygen demand in pounds per hour is calculated.
3. The operating temperature is determined.
4. From the above, the pounds of oxygen transferred per hour can be calculated for a certain oxygen deficit and temperature, to a certain waste. This information can then be converted to pounds of oxygen per hour for any standard condition.

RATING SURFACE AERATORS

Surface aerators are usually rated on the installed horse-power and the oxygen transferred in pounds per hour to pure water with zero DO at 20°C. The quantity of oxygen transferred under actual operating conditions can be found easily by the equation:

$$N = N_o \times \frac{C_{sw} - C}{C_s} \times \frac{1.02^{t-20}}{\alpha}$$

N = Pounds of oxygen transferred to the waste.
 N_o = Pounds transferred to pure water with zero DO at 20°C (usually the rating of the aerator).
 C_{sw} = Saturation value of the waste, ppm.
 C = DO operating level, ppm.
 C_s = Oxygen saturation value of water at 20°C=9.17.
 t = Operating temperature, °C.
 α = Ratio of oxygen transfer to waste to that of water.

If the saturation value of the waste is close to, or equal to, that of water, the effect of temperature change can be obtained from the following table. The results will still have to be multiplied by alpha. For liquids whose saturation value is not the same as pure water, the transfer ratio will have to be computed.

Ratio: O_2 transferred under indicated conditions compared to pure H_2O , at Zero DO at $20^{\circ}C$

OPERATING DO, ppm	<u>T E M P E R A T U R E</u>						
	C° F°	5	10	15	20	25	30
		41	50	59	68	77	86
0		1.04	1.03	.97	1.00	1.04	1.02
1		.96	.94	.88	.89	.92	.88
2		.88	.85	.78	.78	.79	.75
3		.80	.76	.68	.67	.67	.62
4		.72	.68	.59	.56	.54	.48
5		.63	.58	.49	.46	.42	.35

Examples: 1. An aerator can transfer 100 pounds of oxygen per hour to pure water at $20^{\circ}C$ and zero DO. How much will it transfer to pure water at $10^{\circ}C$ and 2 ppm DO?

ANSWER: $100 \times 0.85 = 85$ pounds per hour.

2. If it transfers 100 pounds per hour to water at $5^{\circ}C$ and 3 ppm DO, how much will be transferred at $25^{\circ}C$ and zero DO?

ANSWER: $\frac{100}{.80} = 125$ pounds per hour at zero DO and $20^{\circ}C$

$125 \times 1.04 = 130$ pounds per hour at zero DO and $25^{\circ}C$.

3. A surface aerator is required to transfer 100 pounds of oxygen per hour to a waste at $35^{\circ}C$, with a DO of 2 ppm, an alpha of 0.8, and a DO saturation value 90% that of water. How much oxygen will it transfer to pure water at $20^{\circ}C$ and zero DO?

ANSWER: Sat. DO water at 30°C = 7.63

Sat. DO waste at 30°C =
 $7.63 \times 0.9 = 6.87$

$$100 = \text{No} \times \frac{6.87 - 2.00}{9.17} \times 1.02^{30-20} \times 0.8$$

$$100 = \text{No} \times 0.53 \times 1.22 \times 0.8$$

$$100 = \text{No} \times 0.52 \quad \text{No} = \frac{100}{.52} = 193 \text{ lbs. per hour}$$

COMPARING TEST DATA

General

The ideal testing program would use one tank to test each aerator under the exact same conditions. It would be extremely expensive, however, to maintain a very large tank or lagoon just for testing purposes. Most manufacturers develop the equipment in the laboratory, or in pilot plants, and check the design in a field installation. Field data must be interpreted very carefully if it is to have any meaning.

Mixing

In the discussion of the testing and rating procedure, nothing was said about mixing. It was assumed that the change in DO was uniform throughout the tank so that, no matter where the sample was obtained, the same DO reading would apply.

DO can be measured by standard chemical tests or, more conveniently, by a "probe". This consists of a wand connected by a cable to a box containing batteries and a sensitive ammeter. The probe-end houses two electrodes covered by a thin Teflon membrane. A small potential is applied across the electrodes. When the probe end is placed in a liquid, the current produced is in proportion to the DO of the liquid. The ammeter is calibrated to read percent saturation. If the saturation value is known, then the oxygen deficit can easily be computed.

If the mixing is not complete, the DO readings will be misleading. Plate III illustrates how DO readings can produce a variety of results. This is a section through a lagoon, roughly 475 ft. long by 160 ft. wide, in which three surface aerators are installed. During the test, the middle aerator is inoperative because of a failure in an electrical cable. Lagoon capacity is about 3.5 million gallons of pure water, or 29 million pounds.

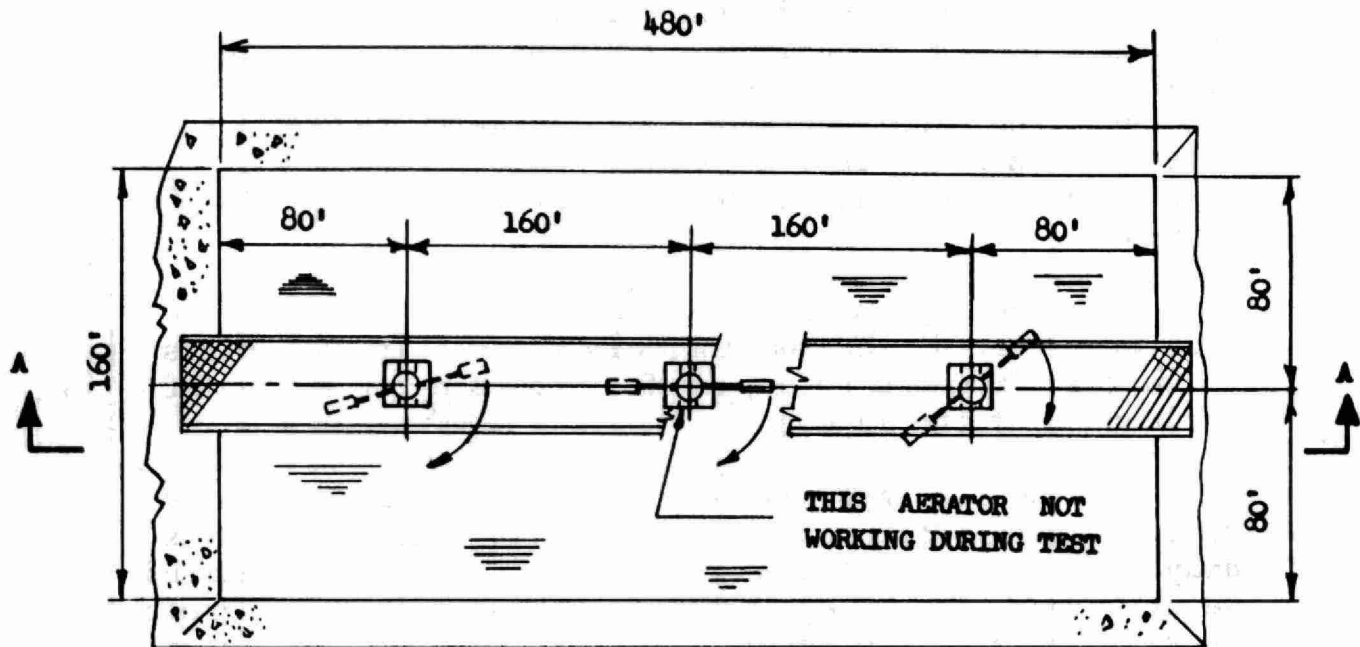
The lagoon is deoxygenated and the two surface aerators started. DO readings are taken at three points - a few feet from one rotor, 40 ft. from one rotor, and at the center of the lagoon.

DO readings will change rapidly near the rotor as the water is sprayed in the air. As this water moves away from the rotor, it becomes diluted with deoxygenated water. Thus, the DO at the 40 ft. point will not increase as rapidly as at the rotor. At the centre of the lagoon, because the third rotor is not operating, the DO will rise slowly. This point is too far from the aerators for proper mixing.

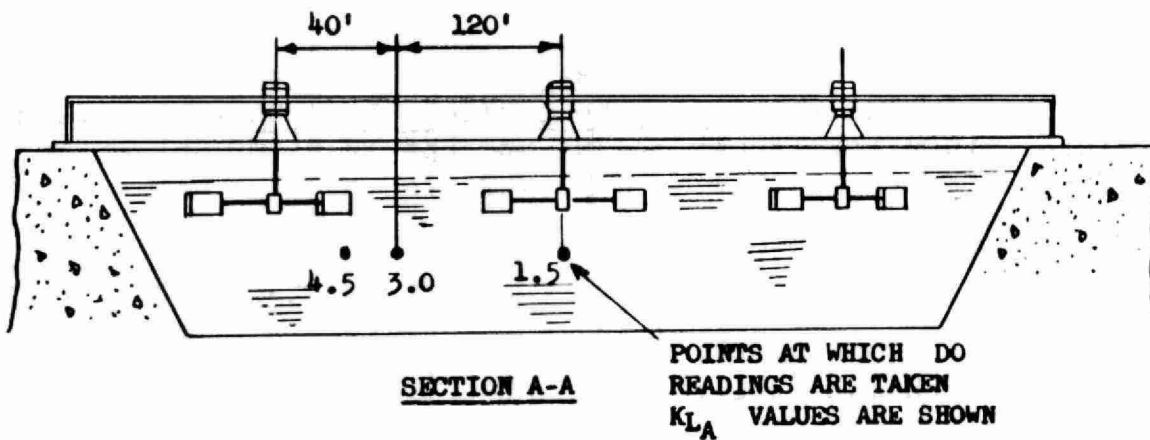
Thus, we can obtain three different K_{LA} values from this test data, as shown on Plate III. The following table shows the pounds of oxygen that will be transferred if each K_{LA} is assumed to be typical throughout the basin. Total drawn horsepower is 20, and operating DO is zero ppm. Oxygen deficit is $9.17 - 0.00 = 9.17$ ppm.

Location	K_{LA}	Oxygen Deficit, ppm	Million Pounds Water	Pounds Oxygen	Pounds Oxygen per Shaft HP
At Rotor	4.5	9.17	2.9	120	6
40' from Rotor	3.0	9.17	2.9	80	4
At Center	1.5	9.17	2.9	20	2

It is clear that if a surface aerator is rated or tested in a lagoon, DO readings will have to be taken at



P L A N
SHOWING LOCATION OF SURFACE AERATORS



LAGOON CAPACITY - 3.5 MILLION GALLONS

LAGOON AERATION
SHOWING EFFECT OF
INCOMPLETE MIXING
ON K_{LA} VALUES
NOT TO SCALE

more than one point or the testing program will not indicate the actual operating results.

Testing in a tank may produce the same type results unless the tank geometry is such that complete mixing is assured. A small, experimental type aerator in a large tank may give misleading ratings when the equipment is scaled-up, unless complete mixing is proven by taking DO readings at different points in the tank.

As a general rule, an aerator sized to transfer enough oxygen to a tank of activated sludge will thoroughly mix the tank contents. This is most important as the sewage, bacteria, and oxygen must all be in intimate contact.

Mixing must be satisfactory in a lagoon, not necessarily complete. For example, there may be a change in the operating DO from 4 ppm at the rotor to 2 ppm at the edge of the lagoon. As long as the minimum is 2 ppm, operation should be good.

A turbine type surface aerator is essentially a low head, high volume pump. It is not possible to measure the quantity of liquid pumped as there is no suction or discharge piping. As the rotor is lowered into the liquid, the horsepower requirements increase to a certain depth, remain fairly constant for a second increment of depth, and then change again as aeration ceases and mixing begins. It can be assumed, therefore, that the increase in energy in the first stage is due to an increase in the amount of liquid pumped, and that mixing is also increased up to the second stage, in which it remains fairly constant.

Oxygen Transfer

A surface aerator replenishes the oxygen consumed by the bacteria during the treatment process. The system is self-balancing. The oxygen demand of the bacteria is dependent on how much sewage they are oxidizing. At night, when sewage flow normally decreases,

the oxygen demand also decreases. Say the system operates with 2 ppm DO during the day, with a total oxygen demand of 100 pounds of oxygen per hour. The aerator will be rated under these conditions. At night the demand may decrease to 80 pounds per hour, so the DO rises to the value of the oxygen deficit at which the aerator will transfer this 80 pounds.

For the above system, more than 100 pounds cannot be transferred with a 2 ppm DO, regardless of the rating of the aerator. The amount transferred must be equal to the demand. If it isn't, the DO will rise until the system is balanced.

Temperature

The temperature correction for the total pounds of oxygen transferred was stated previously as:

$$\text{Pounds at temp. } t = \text{Pounds at } 20^{\circ}\text{C} \times 1.02^{t-20}$$

The constant, 1.02, is commonly used but constants ranging from 1.016 to 1.047 have also been reported. If a surface aerator is rated for oxygen transfer to pure water at 20°C, the selection of the constant may make a significant difference when the data is corrected to, say, 30°C. For example, 100 pounds of oxygen per hour are transferred at 20°C. The following table shows the 30°C corrected value using various constants:

Pounds oxygen per hour at 20°C	Constant	C^{30-20}	Pounds oxygen per hour at 30°C
100#	1.016	1.117	112#
100#	1.020	1.218	122#
100#	1.047	1.580	158#

Thus, when an aerator is to be used at a temperature other than 20°C, the temperature correction constant must be selected with care. The value 1.02 is used by most engineers today.

The above information indicates that surface aerators cannot be selected off the shelf, so to speak. The process, geometry of the basin, and the operating conditions must be evaluated so the surface aerator can be selected to both mix and aerate. A selection based only on pounds of oxygen transferred per hour is not realistic, and may lead to a poor operation of the treatment plant.



THE BANQUET



S. D. FAUST

"FACTORS INFLUENCING THE CONDENSATION
OF 4-AMINOANTIPYRINE WITH PHENOLS"

by

S. D. FAUST

and

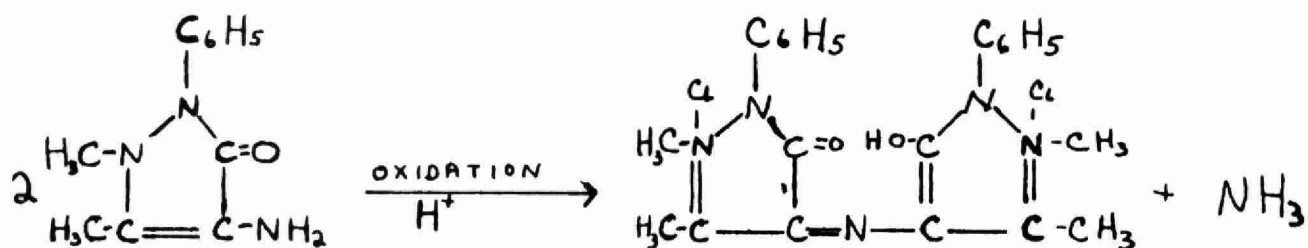
F. C. LORENTZ

Phenolic compounds condense with 4-Amino-antipyrine and by subsequent oxidation under alkaline conditions produced a color the intensity of which is proportional to the phenol concentration. These condensation and oxidation reactions have been applied to the detection and determination of phenols in water and waste waters. Herein are reported the physical and chemical factors influencing these reactions from a critical review of the literature and from our own research.

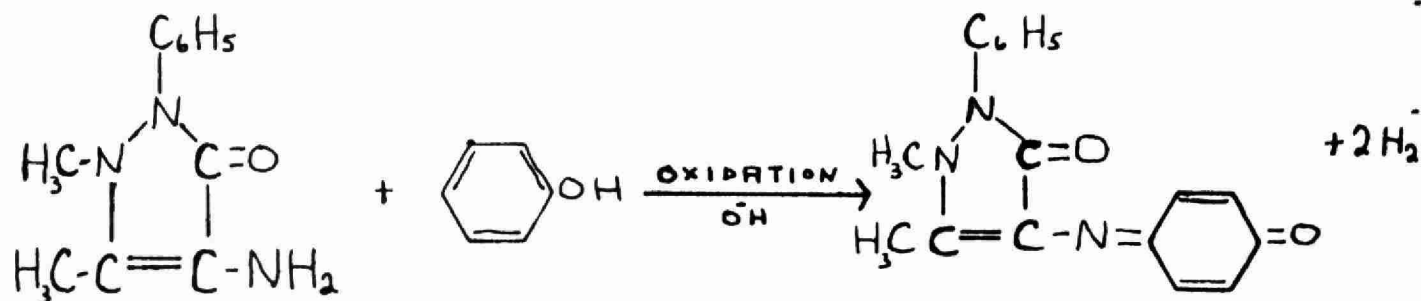
ORIGINAL WORK

Emerson first reported that two moles of aminoantipyrine are condensed and oxidized to antipyrine red under acid conditions with the elimination of one mole of ammonia (reaction 1, figure 1). (1) This reaction was extended to the oxidation of aminoantipyrine in the presence of various aromatic amines to produce indamine-type dyes. Emerson noted also that phenols gave color reactions but under pH conditions entirely different than the amines.

Subsequently, the alkaline oxidation of phenol in the presence of 4-aminoantipyrine by potassium ferricyanide was investigated by Emerson (reaction 2, figure 1. (2) Phenol was detected in



Condensation and Oxidation of 4-Aminoantipyrine



Condensation and Oxidation of the 4-Aminoantipyrine Phenol Complex

Figure 1.

"one part in over eight million, o-cresol in one part in two million, and m-cresol in one part in over six and one-half million." Red to purple colors were produced when the alkalinity was sufficiently high enough to prevent the formation of antipyrine red.

Emerson subsequently investigated the reactivity of a large number of phenols, Tables I and II, from which was concluded:

1. "There must be at least one free phenolic hydroxyl group in the molecule for a positive test."
2. "Substituents in the position para to the hydroxyl group prevent the reaction except as follows: halogen, carboxyl, sulphonic acid, hydroxyl, and methoxyl. These groups are probably expelled."
3. "A nitro group in the ortho position prevents reaction and a nitro group in the meta position inhibits the test but not completely."
4. "Coupling of aminoantipyrine with phenol takes place in the para position rather than in the ortho position."
5. No color reaction occurs when the ortho positions are open and the para position is blocked by alkyl, aryl, ester, nitro, benzoyl, nitroso, or aldehyde groups."

Emerson tried NaOH, NaHCO₃, Na₂CO₃, and NH₄OH to control pH in various empirical combinations with potassium ferricyanide. An absolute pH value was not specified other than to recommend that the system be alkaline enough to prevent formation of the interfering antipyrine red color.

In a subsequent study, Emerson and Kelly again used NaHCO₃, Na₂CO₃, NH₄OH, and NaOH to determine the most satisfactory base (Table III).

TABLE I

<u>PHENOLS REACTING WITH AMINOANTIPYRINE - EMERSON</u> (a)			
<u>Phenol</u>	<u>Reaction</u> (b)	<u>Substitutions on Ring</u>	<u>Position</u>
Phenol	3-S	---	---
o-Cresol	3-S	CH ₃	2
m-Cresol	3-S	CH ₃	3
3,5-Dimethyl-	3-S	CH ₃	3,5
2,5-Dimethyl-	3-S	CH ₃	2,5
Thymol	3-S	CH ₃ , C ₃ H ₇	3,6
Carvacrol	3-S	CH ₃ , C ₃ H ₇	2,5
o-Phenyl-	3-S	C ₆ H ₅	2
o-Cyclohexyl-	3-S	C ₆ H ₁₁	2
o-Hydroxyacetophenone	3-S	COCH ₃	2
2,4'-Dihydroxybenzophenone	3-Ins.	COC ₆ H ₅ OH	2
3,Methyl, 4-Chloro-	3-S	CH ₃ Cl	3,4
o-Chloro-	3-S	Cl	2
p-Chloro -	3-S	Cl	4
2,4-Dichloro-	3-S	Cl, Cl	2,4
p-Bromo-	3-S	Br	4
2,6-Dibromo-	3-S	Br, Br	2,6
2,4,6-Tribromo-	3-S	Br, Br, Br	2,4,6
m-Methoxy-	3-S	OCH ₃	3

Table I, Cont'd.

<u>Phenol</u>	<u>Reaction</u>	(b)Substitutions <u>on Ring</u>	<u>Position</u>
p-Methoxy-	3-S	OCH ₃	4
Guaiacol K Sulphonate	3-Ins.	OCH ₃ , SO ₃ K	2,6
o-Phenolsulphonic acid	3-Ins.	SO ₃ H	2
p-Phenolsulphonic acid	3-S	SO ₃ H	4
o-Carboxyl-	3-Ins.	COOH	2
m-Carboxyl-	3-Ins.	COOH	3
p-Carboxyl-	3-S	COOH	4
Methyl Salicylate	3-S	COOCH ₃	2
Salol	3-S	COOC ₅ H ₅	2
Salicylsalicylic acid	3-SSI	COOC ₆ H ₄ COOH(o)	2
Salicylanide	3-S	CONH ₂	2
Salcylaldehyde	3-S	CHO	2
3,Methoxy, 4-Carboxyl-	3-S	OCH ₃ , COON	2,4
2,6-Dibromo, 6-Carboxyl-	3-S	Br, COOH, Br	2,4,6
o-Hydroxy-	3-Ins.	OH	2
m-Hydroxy-	3-Ins.	OH	3
p-Hydroxy-	1-S	OH	4
3,Hydroxy, 5-Methyl-	3-Ins.	OH, CH ₃	3,5
4-Tert. Butylcatechol	1-S	OH, C ₃ H ₇	2,5
3,5-Dihydroxy-	3-Ins.	OH, OH	3,5
2,3-Dihydroxy-	3-Ins.	OH, OH	2,3

Table I, Cont'd.

<u>Phenol</u>	(b) Substitutions		<u>Position</u>
	<u>Reaction</u>	<u>on Rings</u>	
m-Nitro-	2-S	NO ₂	3
m-Amino-	3-S	NH ₂	3

(a) Reference 2

(b) 3, strong test; 2, moderate test; 1, slight test;
S, soluble; Ins, insoluble; SS1, slightly
soluble.

TABLE II

PHENOLS NOT REACTING WITH AMINOANTIPYRINE - EMERSON (a)

<u>Compound</u>	<u>Substitutions on Ring</u>	<u>Position</u>
Anisole	OCH ₃	1
p-Cresol	CH ₃	4
2,4-Dimethyl-	CH ₃ , CH ₃	2,4
2,4-Dimethyl-	CH ₃ , CH ₃	3,4
p-Tert. Amyl-	C ₅ H ₁₁	4
p-Tert. Butyl-	C ₄ H ₉	4
p-Tert. Butyl-o-cresol	CH ₃ , C ₄ H ₉	2,4
p-Tert. Amyl-o-cresol	CH ₃ , C ₅ H ₁₁	2,4
4-Phenyl-	C ₆ H ₅	4
p-Cyclohexyl-	C ₆ H ₁₁	4
Tyrosine	CH ₂ NH ₂ COOH	4
p-Hydroxyacetophenone	COCH ₃	4
4,4'-Dihydroxybenzophenone	COC ₆ H ₄ OH	4
o-Methoxy-	OCH ₃	2
Eugenol	OCH ₃ , CH ₂ CH:CH ₂	2,4
iso-Eugenol	OCH ₃ , CH:CHCH ₃	2,4
Methyl p-hydroxybenzoate	COOCH ₃	4
p-Hydroxybenzaldehyde	CHO	4
Vanillin	OCH ₃ , CHO	2,4
o-Nitro-	NO ₂	2

Table II, Cont'd.

<u>Compound</u>	<u>Substitutions on Ring</u>	<u>Position</u>
p-Nitro-	NO ₂	4
p-Nitroso-	NO	4
p-Amino-	NH ₂	4

(a) Reference 2.

TABLE III

EFFECT OF EXCESS BASES ON THE CONDENSATION REACTION
OF PHENOLS WITH 4-AMINOANTIPYRINE (a)

Base	NaHCO ₃ -0.17M					Na ₂ CO ₃ -0.08M					NH ₄ OH -0.17M					NaCl -0.17M				
Drops Used	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
<u>Compounds</u>																				
Phenol	3 ^(b)	3	2	2	2	3	3	2	2	2	3	3	3	3	3	3	3	2	1	1
2,4-Dichloro-	5	5	5	5	5	5	5	3	3	2	5	5	3	3	3	2	1	-	-	-
2,4,6-Tribromo-	5	5	5	5	5	5	5	1	1	1	5	5	1	1	1	5	-	-	-	-
o-Nitro-	3	3	3	3	2	3	-	-	-	-	3	-	-	-	-	-	-	-	-	-
m-Nitro-	1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
m-Carboxyl-	1	2	2	2	2	3	3	3	2	2	3	3	3	3	2	2	1	1	1	1
o-Chloro-	5	5	5	5	5	5	5	5	5	3	5	5	5	5	5	5	1	1	-	-
3,5-Dimethyl-	3	4	4	2	2	3	2	2	2	2	1	3	3	2	2	3	2	2	2	2
p-Carboxyl	2	3	3	2	2	3	2	2	2	2	3	3	3	3	2	2	1	1	1	1

(a) Reference 3

(b) Arbitrary color intensity scale: 5 indicates a precipitate was formed, 4, a very intense color, 1, a very weak test.

In general, color formation is dependent upon amount of base, type of base, and type of phenol. The bases, when used in excess, can be arranged in a series of increasing inhibition: NaHCO_3 NH_4OH Na_2CO_3 NaOH . Emerson suggested, therefore, that NaHCO_3 be used as the alkaline agent. Also, the data in Table III indicate that: (a) different phenols have different sensitivities of reaction with 4-aminoantipyrine, (b) pH or ionic strength affects color intensity, (c) some phenols exhibit a pH effect on maximum color formation as evidenced by 3,5-dimethyl phenol and p-carboxyl phenol, and (d) phenols that have groups expelled from the para position are inhibited more by excess base.

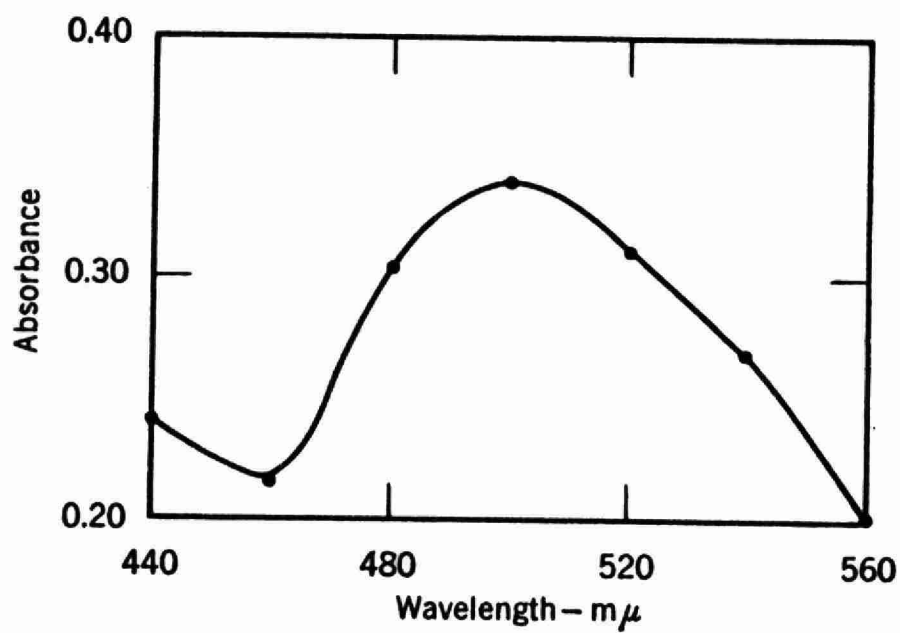
WAVE LENGTH OF MAXIMUM ABSORBANCE

Table IV shows the wave lengths of maximum absorbance for several phenols as determined by several investigators (4,5,6,7,8) and from our own research. These values ranged from 495 to 550 mμ and generally exhibited broad spectra as exemplified by 2,4-dichlorophenol in Figure 2. (4) pH value and type of buffer appear to influence wave length of maximum absorbance for a given phenol.

EFFECT OF pH ON ABSORBANCE

Since the original data of Emerson suggested that pH affects color intensity and that the pH should be high enough to prevent development of the antipyrine red color, several analytical methods were developed at a pH value of 10.0. Gottlieb and Marsh, using a sodium carbonate buffer, effected the reaction at pH 10.4-10.6. (5) Ettinger, et al., suggested a pH range of 9.8-10.2 controlled by a 6N NH_4OH solution, (6) and Standard Methods recommends an NH_4OH - NH_4Cl buffer at pH 10.0 ± 0.2 . (9)

Subsequently, an investigation revealed that at the pH value of 10.0 ± 0.2 , 2,4-dichlorophenol produced very little color, whereas at pH 7.9 ± 0.1 maximum intensity was developed. Since these results were contrary to those of Gottlieb and Marsh (5) who reported



**Absorbance Curve for the 2,4-Dichlorophenol -
4-Aminoantipyrine Complex**

Figure 2.

TABLE IV

WAVE LENGTH OF MAXIMUM ABSORBANCE OF SEVERAL
PHENOL-4-AMINO ANTIPYRINE COLOR COMPLEXES

<u>Phenol</u>	<u>Max - m^(a)</u>	<u>Reported pH Value</u>	<u>Buffer System</u>	<u>Reference</u>
2,4-Dichloro-	500	7.9	NH ₄ OH-PO ₄	4
2,4-Dichloro-	510	10.4	Na ₂ CO ₃	5
2,4-Dichloro-	510 ^(b)	10.0	NH ₄ OH	6
o-Cresol	510 ^(b)	10.0	NH ₄ OH	6
m-Cresol	510 ^(b)	10.0	NH ₄ OH	6
o-Chloro-	510 ^(b)	10.0	NH ₄ OH	6
p-Chloro-	510 ^(b)	10.0	NH ₄ OH	6
2,4,6-Trichloro-	510 ^(b)	10.0	NH ₄ OH	6
Phenol	510 ^(b)	10.0	NH ₄ OH	6
Phenol	505	9.2	H ₃ BO ₃ -NaOH	7
Phenol	540	10.1	Na ₂ B ₄ O ₇	8
Phenol	500	9.0-10.6	KH ₂ PO ₄ -NaOH	8
Phenol	500	10.5	Na ₂ CO ₃	8
Phenol	500 ^(c)	8.0	NH ₄ OH-PO ₄	-
p-Methoxy-	500 ^(c)	8.0	NH ₄ OH-PO ₄	-
p-Chloro-	500 ^(c)	8.0	NH ₄ OH-PO ₄	-
p-Bromo-	500 ^(c)	8.0	NH ₄ OH-PO ₄	-
p-Ethoxy-	500 ^(c)	8.0	NH ₄ OH-PO ₄	-

Table IV, Cont'd.

<u>Phenol</u>	<u>Max - μ</u> ^(a)	<u>Reported pH Value</u>	<u>Buffer System</u>	<u>Reference</u>
2,4,5-Trichloro-	500 ^(c)	8.0	NH ₄ OH-PO ₄	-
2,4,6-Trichloro	500 ^(c)	8.0	NH ₄ OH-PO ₄	-
4-Chloro-3,5-Dimethyl-	550 ^(c)	8.0	NH ₄ OH-PO ₄	-
Pentabromo-	520 ^(c)	8.0	NH ₄ OH-PO ₄	-

(a) Aqueous systems. (b) Shifted to 460 μ in CHCl₃.
(c) Spectronic 20, 2.40 cm cells.

TABLE V

EFFECT OF DIFFERENT BUFFERS ON pH STABILITY
OF THE REACTION MEDIUM

<u>Ammonium Hydroxide- Phosphate</u>		<u>Ammonium Hydroxide- Ammonium Chloride</u>		<u>Ammonium Hydroxide</u>	
<u>Before</u>	<u>After</u>	<u>Before</u>	<u>After</u>	<u>Before</u>	<u>After</u>
pH	pH	pH	pH	pH	pH
7.6	7.6	8.0	7.8	9.5	8.8
8.0	8.0	8.5	8.3	9.6	9.1
8.5	8.45	9.0	8.8	9.8	9.3
9.0	8.95	9.5	9.3	10.0	9.7
9.5	9.45	10.0	9.8	10.2	9.9
10.0	9.95			10.7	10.4

that 2,4-dichlorophenol was determined at pH 10.4 with a Na_2CO_3 buffer, their procedure was repeated: the initial pH of the reaction system was 10.4 but after the 4-aminoantipyrine and $\text{K}_3\text{Fe}(\text{CN})_6$ reagent were added, the pH fell to 7.9. These results agree with Dannis (10) who also observed the effect of reagent addition on final pH value in an $\text{NH}_4\text{OH-NH}_4\text{Cl}$ buffer system. Consequently, the effect of three aqueous buffers on pH stability of the reaction medium was investigated (Table V). The $\text{NH}_4\text{OH-PO}_4$ system provided the greatest stability.

That pH value does affect absorbance readings of phenol-4-aminoantipyrine color complexes is seen in Table VI. In general, as pH was increased from 8.0 to 10.5, absorbance values decreased, the magnitude of which varied with each phenol. For example, the absorbance for 2,4-dichlorophenol decreased from 0.229 to 0.022, whereas for phenol the decrease was from 0.222 to 0.174. Substitution on the phenol ring also apparently affects the reactivity with 4-aminoantipyrine at the higher pH values. This can be seen by comparing the absorbance readings of the tri-substituted phenols with those of the mono- and di-substituted. These results are in general agreement with those of Emerson (Table III).

Type of buffer is another factor influencing color intensity. Different transmittance values are given for 2,4-dichlorophenol at a given pH value with three different buffers, (Figure 3). The NH_4OH buffer gave the highest color intensity at a given pH value but did not provide stability against pH drop as noted in Table V.

La Coste, et al., also noted the effect of pH and buffer type on color intensity that was ascribed to variations in ionic strength. (7) Their data are summarized in Table VII from which absorbance values: (a) vary inversely with ionic strength at any pH value as noted by the $\text{NH}_4\text{OH-NH}_4\text{Cl}$ systems, (b) differ with type of buffer, and (c) decrease as pH value increases. LaCoste suggested that variations in color intensity due to ionic strength is a specific ion effect; namely, the ammonium ion which is demonstrated by comparison of the absorbance data from the NaOH-HCl systems with the 1.0M $\text{NH}_4\text{OH-NH}_4\text{Cl}$ and $\text{NH}_4\text{OH-NH}_4\text{Ac}$ buffers. LaCoste

TABLE VI

EFFECT OF pH VALUE ON ABSORBANCE OF SEVERAL
PHENOL-4-AMINOANTIPYRINE COLOR COMPLEXES

Phenol ^(a)	pH Value ^(b)					
	8.0	8.5	9.0	9.5	10.0	10.5
	Absorbance ^(c)					
Reagent Blank	0.022	0.013	0.009	0.018	0.009	0.004
Phenol	0.222	0.208	0.187	0.131	0.194	0.174
Phenol ^(d)	0.360	0.360	0.360	0.360	0.360	0.340
p-Methoxy-	0.149	0.137	0.125	0.114	0.125	0.131
b-Bromo-	0.119	0.114	0.065	0.046	0.046	0.046
2,4-Dichloro-	0.229	0.125	0.081	0.051	0.041	0.022
2,4,5-Trichloro-	0.222	0.131	0.071	0.036	0.022	0.013
2,4,6-Trichloro-	0.143	0.081	0.032	0.018	0.009	0.004
4-Chloro-3,5-Dimethyl-	0.131	0.103	0.081	0.065	0.055	0.051

(a) 50 ug

(b) $\text{NH}_4\text{OH-PO}_4$ buffer systems

(c) Distilled Water blank, 500 mu, $20^\circ \pm 0.5^\circ\text{C.}$, 2.40 cm cells

(d) From ref. 10., 500 ug, 520 mu, $\text{NH}_4\text{OH-NH}_4\text{Cl}$ buffer

TABLE VII

EFFECT OF pH AND IONIC STRENGTH ON ABSORBANCE

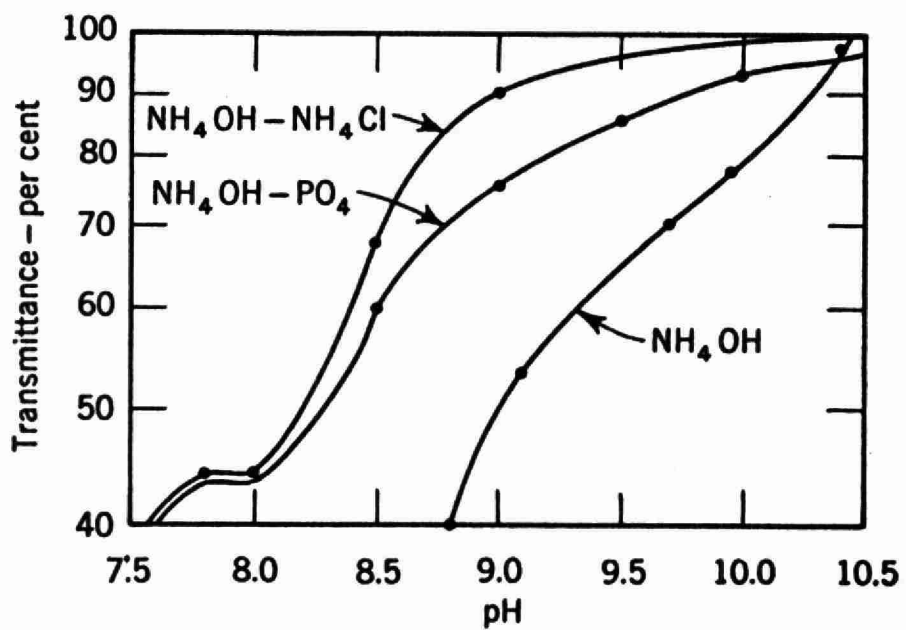
(a)
(b)
ABSORBANCE READINGS

pH	<u>NH₄OH-NH₄Cl</u>				<u>NH₄OH-NH₄Ac</u>	<u>NaOH-HCl</u>		<u>H₃CO₃-NaOH</u>
	<u>0.1M</u>	<u>0.5M</u>	<u>1.0M</u>	<u>1.5M</u>	<u>1.0M</u>	<u>0.1M</u>	<u>.0M</u>	<u>0.4M</u>
8.0	--	--	--	--	0.160	0.470 ^(c)	--	0.420 ^(c)
8.2	0.410	--	--	--	--	--	--	--
9.0	--	--	--	--	0.220	--	--	0.420
9.5	0.410	0.300	0.230	0.100	--	0.450	0 460	0.420
10.0	--	0.330	0.220	0.120	0.250	--	0 450	0.420
10.5	0.440	0.350	0.280	0.140	--	0.400	0 400	0.350
11.0	--	--	--	--	--	0.280	0 320	0.280
12.0	--	--	--	--	--	0.050	0 040	0.030

(a) Reference 7.

(b) Phenol Conc. = 3.3 mg/l.

(c) Phenol Conc. = 3.0 mg/l.



Effect of Type of Buffer on Color Intensity of the 2,4-Dichlorophenol Color Complex

Figure 3.

chose the NaOH-H₃BO₃ system because "constant color intensity was recorded in the pH range of 8.2 to 10.0 and color intensity is essentially constant at pH 9.2 with ionic strengths of 0.02, 0.2, and 1.0M boric acid." These data and conclusions should be examined, however, with criticism, because no mention was made of the effect of reagent addition on pH stability of the various buffers. The variations in absorbance readings, Table VII, may be due to variations in the final pH of the reaction mixtures.

Ochynski compared color intensity development in borate, phosphate, and carbonate buffers.⁽⁸⁾ A portion of these data is seen in Table VIII from which Ochynski concluded: "maximum colour formation for a given concentration of phenol occurs at a pH between 9 and 10.7 and that the chemical composition of the buffer solution has no effect on the light absorption." These conclusions are somewhat in variance with LaCoste,⁽⁷⁾ and Faust and Aly⁽⁴⁾ but were made from only three buffer systems in which NaOH or Na⁺ was the predominant base.

EFFECT OF TYPE OF PHENOL

The earlier work of Emerson suggested that type of phenol and type of substitution in the o, m, and p positions affects the degree of reactivity with 4-aminoantipyrine (Tables I, II, and III). Since these data were qualitative, there was no indication of the molecular and analytical sensitivities of these phenols. Table IX shows that analytical and molecular sensitivities vary directly with absorptivity value. In general, these data are in agreement with Emerson, with the exception of 4-methyl-, 3,4-dimethyl-, and 4-phenyl phenol that exhibit some reactivity but low sensitivities.

Substitution on the phenol ring greatly influences the reaction with 4-aminoantipyrine. In group 1, where the para position is open, reaction sensitivity decreases as the number of substitutions increases. In groups 2,3,4,5, and 6, the type of the para substitution as well as that of the ortho and meta groups influences reactivity. In general, halogen groups enhance reactivity whereas alkyl groups suppress reactivity.

TABLE VIII

LIGHT-ABSORPTION VALUES IN PRESENCE OF BORATE,
PHOSPHATE, AND CARBONATE SOLUTIONS^(a)

<u>pH</u>	<u>Absorptiometer-Drum Units</u>	
	<u>0.1M NaOH-H₃BO₃</u>	
9.0	0.12 ^(b)	0.23 ^(c)
9.6	0.12	0.23
10.0	0.11	0.22
10.6	0.12	0.23
<u>0.1M NaOH-KH₂PO₄</u>		
7.7	0.08	0.22
9.2	0.13	0.24
10.7	0.13	0.25
11.0	0.10	0.20
11.5	0.08	0.15
<u>0.1M Na₃CO₃</u>		
10.5	0.11	0.21

(a) Reference 8.

(b) Phenol Conc. = 2.0 mg/l.

(c) Phenol Conc. = 4.0 mg/l.

TABLE IX

EFFECT OF TYPE OF PHENOL ON ABSORPTIVITY VALUES

<u>Group</u>	<u>Para Substitution</u>	<u>Phenol (a)</u>	<u>Molar Absorptivity</u>	<u>Absorptivity</u>
1	H	3-Chloro-	13,500	105.0
	"	Phenol	9,310	98.9
	"	3-Methoxy-	10,100	81.4
	"	2,6-Dimethyl-	5,210	42.6
	"	3,5-Dimethyl-	3,810	31.2
	"	2-Isopropyl,5-Methyl-	2,810	18.7
2	Cl	2,4-Dichloro-	14,300	97.5
	"	2,4,5-Trichloro-	11,200	56.4
	"	2,4,6-Trichloro-	10,500	52.6
	"	4-Chloro-	6,770	52.6
	"	4-Chloro,3,5-Dimethyl-	4,400	27.9
3	Alkyloxy	4-Methoxy-	7,330	61.6
	"	4-Ethoxy-	5,730	41.6
4	Alkyl	4-Methyl-	54.5	0.504
	"	3,4-Dimethyl-	224	1.84
	"	2-Amino,4-Phenyl-	846	4.5
	"	4-Phenyl-	41.2	0.242
5	Amino	4-Amino,3-Methyl-	972	7.91
	"	4-Amino,2,6-Dibromo-	2,480	9.23
6	Br	4-Bromo-	6,230	36.1

(a) 500 mu, 2.24 cm cells, $20^{\circ} \pm 0.5^{\circ}\text{C.}$, pH 8.0 ± 0.1 , reagent blank.

Variations in the sensitivity of different phenols were observed also by Dannis⁽¹⁰⁾, Ettinger⁽⁶⁾, and Mohler and Jacob⁽¹¹⁾.

EFFECT OF INTERFERENCES

Interferences with the 4-aminoantipyrine and phenol reaction fall into three general types: (a) red color from the oxidation of 4-aminoantipyrine, (b) inorganic reducing substances, and (c) aromatic amines that also condense with 4-aminoantipyrine. Antipyrine red can be eliminated by keeping the reaction pH value above 7.4 as indicated in Table X.

Inorganic sulphides, such as Na_2S , interfere by reaction with the oxidizing agent as quantitated by Gordon⁽¹²⁾ (Table XI). This interference has been eliminated by precipitation with CuSO_4 ⁽⁹⁾ or AgNO_3 ⁽¹²⁾ and by acid extraction of the sample with petroleum ether.⁽⁴⁾

Ettinger observed that aniline produced a color with 4-aminoantipyrine that decreased in intensity as the pH value was increased from 9.6 to 11.15 (Table XI).⁽⁶⁾ Consequently, a pH range of 9.8 to 10.2 was suggested that would minimize this interference since 20 mg/l of aniline are equivalent to 0.1 mg/l phenol in absorbance values. Aromatic amines were eliminated also by an acid petroleum extraction technique.⁽⁴⁾ Aniline did not interfere up to 20 mg/l by this procedure.

McFarlane observed interferences from colloiddally dispersed or suspended organic matter in paper and pulp mill effluents.⁽¹³⁾

EFFECT OF TEMPERATURE

The effect of temperature on absorbance values from various 4-aminoantipyrine-phenol color complexes has been documented well by Ettinger⁽⁶⁾, Ochynski⁽⁸⁾, and LaCoste⁽⁷⁾. Ettinger found that a 37°C. temperature gave lower absorbance readings than 20°C. which was

TABLE X

EFFECT OF pH VALUE ON ANTIPYRINE RED FORMATION

<u>pH</u>	<u>Color Formed</u>	<u>Time After Which Fading Began (Min.)</u>
5.8	Deep Red	30
6.0	" "	30
6.5	" "	30
7.0	Moderate Red	15
7.2	Slightly Red	5
7.4	No Red	-
7.6	" "	-
7.8	" "	-

TABLE XI

EFFECT OF SULPHIDES^(a) AND ANILINE^(b)

<u>Na₂S</u>	<u>Phenol^(c)</u>	<u>pH</u>	<u>Aniline</u>
mg/l	mg/l		Absorbance ^(d)
0	4.0	9.6	0.85
10	3.7	9.8	0.50
20	3.5	9.9	0.45
40	2.4	10.1	0.30
60	0	10.5	0.15
80	0	11.15	0.05

(a) Reference 12.

(b) Reference 6.

(c) 510 mu.

(d) 100 mg/l aniline, 460 mu in CHCl₃, 1.0 cm.

attributed to color fading. Ettinger also found a higher absorbance reading for the reagent blank at 37°C. than at 20°C. Ochynski, however, reported temperatures of 25° to 50°C. did not affect the absorbance value of 18 mg/l phenol but that the color faded over 50°C. Likewise, LaCoste observed no appreciable effects on any given phenol concentration over the temperature range of 16° to 36°C.

EFFECT OF ORDER OF REAGENT ADDITION AND REAGENT CONCENTRATION

Ettinger suggested that the following order of reagent addition to the phenol shall be: (a) pH buffer, (b) 4-aminoantipyrine, and (c) oxidizing agent.⁽⁶⁾ This indicates that the color reaction occurs in the following sequence: (a) ionization of the phenol, (b) condensation with the phenol, and (c) oxidation to the quinoid structure. That the color producing reagents be added in excess was determined by Ettinger⁽⁶⁾ and LaCoste⁽⁷⁾.

EFFECT OF COLOR-COMPLEX STABILITY

There are mild disagreements relative to the stability of color complex (Table XII). Ettinger's data⁽⁶⁾ suggested a slow fading over 120 minutes with phenol, whereas Ochynski's data⁽⁸⁾ did not. LaCoste found considerable fading of the MEHQ color complex over 25 minutes and within two temperature ranges.⁽⁷⁾

Table XIII shows the effect of time on stability of the 2,4-dichlorophenol color complex at pH 8.0. Maximum absorbance was developed within 15 minutes and remained stable for at least two hours.

DISCUSSION

The condensation of phenols with 4-aminoantipyrine with subsequent alkaline oxidation to a colored product appears to be two simple, straightforward chemical reactions. When these reactions are quantitated, however, several

TABLE XII

STABILITY OF COLOR-COMPLEXES IN AQUEOUS SOLUTION

<u>Time</u> <u>Min.</u>	<u>Phenol^(a)</u> <u>0/6 mg/l</u>	<u>Phenol^(b)</u> <u>2.0 mg/l</u>	<u>MEHQ^(c)</u>	<u>MEHQ^(c)</u>
ABSORBANCE VALUES				
0.0	0.37	----	0.310	0.295
5.0	----	0.11	0.300	0.275
10.0	----	----	0.285	0.255
15.0	0.36	----	-----	-----
20.0	----	----	0.275	0.245
25.0	----	----	0.275	0.245
30.0	0.35	----	-----	-----
45.0	0.34	----	-----	-----
60.0	0.33	----	-----	-----
120.0	0.32	----	-----	-----
150.0	----	0.10	-----	-----
<u>Temp.</u>	Room	Room	24-25°C.	35-36°C.
<u>pH</u>	9.8-10.1	9.0-10.7	9.2	9.2

(a) Reference 6, 520 mu, 5.0 cm.

(b) Reference 8, 540 mu.

(c) Reference 7, monomethyl ether of hydroquinone,
505 mu, 1.00 cm.

TABLE XIII

EFFECT OF TIME ON STABILITY OF THE COLOR COMPLEX AT pH 8.0^(a)

2,4-Dichlorophenol

Absorbance^(b)

<u>ug</u>	<u>15 min.</u>	<u>60 min.</u>	<u>120 min.</u>
10	0.043	0.043	0.041
30	0.114	0.114	0.111
50	0.187	0.187	0.180
80	0.288	0.288	0.284
100	0.357	0.357	0.347

(a) Reference 4.

(b) 500 mu, 2.3 cm., room temperature.

factors have to be considered. First, the pH value between 8.0 and 11.0 and type of buffer influence greatly the reactions. These two factors determine the absorbance value, wave length of maximum absorption, and the sensitivity with which a particular phenol will react. Also, the position, type, and number of substitutions on the phenol ring influence the sensitivity of the reaction. Substitution in the ortho and meta positions suppresses the reactions. Substitution in the para position by alkyl, aryl, ester, nitro, benzoyl, nitroso, amino, and aldehyde appears to block and/or inhibit the reactions, the degree of which is influenced by the pH value. Other factors of interferences, color complex stability, temperature, and order of reagent addition are eliminated or standardized by conventional analytical techniques.

Critical evaluation of the above factors relative to an analytical technique suggests that only an approximation can be made of the phenol content of a water or waste water. A "total phenol" content is not possible with the 4-aminoantipyrine method since many phenols are weakly reactive or do not react at all. Sufficient data are available, however, to show that a closer approximation of the total phenol content can be obtained at a reaction pH of 8.0 than at 10.0. At pH 8.0, a greater number of the para-substituted phenols react.

Presumably, the reaction occurs as a coupling of the 4-aminoantipyrine at the para position of the phenol. This has never been directly established through a mechanism study. A para-condensation on the phenol ring is logical, however, since the OH substitution is ortho and para directing. Also, a para-condensation is required for a quinoid structure to appear upon oxidation. Consequently, the reactivity of substituted phenols is determined by the combined influence of the groups that activate or deactivate the para-position. In general, the phenols that are substituted with ortho and para-directing groups appear to be more reactive than those with meta directing groups.

SUMMARY

The quantitative determination of phenols in water and waste water is attempted by condensation with 4-aminoantipyrine and oxidation under alkaline conditions to a colored product. The major chemical factors that influence this reaction are pH value between 8.0 and 11.0, the type of aqueous buffer, and the type of substituted phenol. These three factors influence the analytical and molecular sensitivities as well as the wave length of maximum absorbance. A "total phenol" determination is not possible with the 4-aminoantipyrine technique as currently practiced.

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AFTER DINNER
SPEAKERS





"IRRIGATION AND LAND DISPOSAL
OF PULP MILL EFFLUENTS"

by

R. O. BLOSSER

and

E. L. OWENS

R. O. BLOSSER

The use of the land for disposal of various organic effluents has been of growing interest in recent years. Methods evolved have ranged from seepage ponds or direct application to the soil, with irrigation of little or minor importance, to closely controlled effluent application designed to produce agricultural crops.

While disposal of sanitary sewage by this means has a long history, progress in its use for industrial effluents is of more recent date. Industrial application of the practice of land disposal has been most rapid in the food processing industry. McKee/1/, Schraufnager/2/, Sanborn/3/, Rohlich/4/, and Monson/5/ have reported on a great number of these installations employing principles of spray or ridge and furrow irrigation for the disposal of cannery, milk processing and cheese manufacturing operations, while Scott/6/ recently reviewed in some detail the land disposal of organic effluent in Wisconsin.

In 1959 a survey of the pulp and paper industry revealed that 21 mills had investigated, or were practicing either in pilot or full scale, some form of land disposal. That interest continues to be exhibited in these areas is reflected in current activity, and 27 mills are experimenting with or practicing some form of land disposal.

Several factors favor the use of land disposal, among these being location of some plants in agricultural areas and seasonal operations such as occur in food processing. The seasonal nature of the effluent disposal problem itself is, however, of great importance. While most pulp and paper mills operate the year around producing an effluent of uniform volume and strength, many are located on streams with well defined low-flow patterns of limited duration. In many cases adequate self-purification capacity is available except during the short low-flow periods during the summer months. The problems associated with the onset of low flow are accentuated in some areas with the seasonal increase in irrigation practice which substantially reduces the available runoff.

Of primary significance in acceptance of land disposal practices has been the rising cost of waste treatment facilities. While many effluents can be successfully treated by conventional trickling filters, activated sludge or modifications thereof, the cost for construction is high.

Despite the conditions which appear to make land disposal another tool in the field of waste disposal, some attempts of application have met with only partial success and others with failure. The National Council, therefore, undertook a basic study of land disposal to determine the effect of soil characteristics on its capacity for treatment of various pulp mill effluents, the effect of cover vegetation on soil treatment capacity, the effect of effluent composition on soil characteristics, fertilizing or soil conditioning effects of effluents, if any, or possible adverse effect on ground water quality where highly coloured effluents are applied as irrigation water.

The laboratory studies have dealt with changes in effluent characteristics, changes in soil characteristics, and changes in cover vegetation conditions when a wide variety of effluents are applied to the soil in simulated irrigation practice. The initial phases of the investigation dealt with changes occurring when effluents were applied to bare soil columns similar to those shown in

Fig. 1. The study was then expanded to investigate the role of cover vegetation on the land in irrigation disposal of pulp and papermill effluents. Figure 2 is a view of the greenhouse showing some of the laboratory columns used in this portion of the study. The cover vegetation is *alta fescue*, a grass of high moisture resistance and reasonably high salt tolerance with an extensive root formation. These qualities make it well suited for use in irrigation disposal operations where maximum water application is desirable, and it has proven to be superior to Reed canary grass in the laboratory investigations.

Four representative soils have been used in these studies; a sand loam, a silt loam, and two clay loams; classifications which principally define particle size. Their ion exchange capacity, or capacity to chemically adsorb the cations, also differs, increasing with decreasing particle size, with the clays having the highest exchange capacity. Analyses employed have included BOD, colour, pH, lignin, conductivity, and measurement of the cations and anions of major importance in soil management to include sodium, calcium, magnesium, potassium, sulphates, and chlorides. Percolate collection and measurement have afforded the opportunity to establish moisture loss by evapotranspiration, while clipping of the grass at regular intervals, where cover vegetation is employed, provides a measure of productivity which reflects the benefit or apparent harm to the cover vegetation by a specific effluent or set of conditions. Volumetric loadings of 5 to 11 inches per week, or 20,000 or 43,000 gallons per acre day, have been used where cover vegetation is employed. This hydraulic load is in excess of the consumptive requirements of the cover vegetation in the laboratory and simulates field conditions where application rates of about 9,000 gallons per acre day in the northern latitudes are in excess of evapotranspiration requirements and would result in percolation to the ground water.

Extended irrigation periods of 9 months or longer, representing in many areas the equivalent of 2 to 3 years seasonal effluent disposal, have been employed to assist in evaluating long term effects. Subsequent to the irrigation period, the soils are leached with tap water

to simulate a period of high precipitation following seasonal disposal. A number of effluents to include bleached kraft, unbleached kraft, kraft recovery condensates, caustic extract wash water, dilute solutions of kraft black liquor, insulating board mill, sulphite, kraft effluents fortified with sodium or wood sugars, and other synthetic effluents, as well as tap water, have been employed to cover the wide spectra of effluent characteristics encountered at field installations.

BOD REDUCTION IN THE SOIL

BOD has been one of the parameters of evaluation used to measure the change in mill effluent characteristics as they percolate through soil. When observing the soil percolate from columns loaded at different BOD levels it has been possible to identify significant changes in soil percolate quality. These changes are directly identifiable with the organic loading applied when expressed as a function of the soil surface BOD loading.

At loadings of up to 235 pounds BOD per acre day, reductions of 95 per cent or greater have consistently been recorded with no impairment of cover vegetation or soil permeability reduction assignable to rapidly decomposable organic matter. Removals of 60 to 84 per cent were noted at loadings of 280 pounds per acre day with accompanying septic percolate. Both illustrate that insufficient oxygen was gaining entry at the soil surface to maintain aerobic conditions. Excessive cover vegetation damage, finally resulting in complete kill, as well as reduced soil permeability, were also noted after 8 months of irrigation. BOD loads just over 400 pounds per acre per day also were reduced about 60 per cent. Impairment of grass growth was more rapid and severe, however, finally resulting in reduced soil permeability and, hence, mandatory lower hydraulic loadings by the end of the third month of effluent application. These findings are illustrated in Table 1.

The high degree of treatment afforded at loadings less than 235 pounds per acre per day has been found to be independent of soil or effluent type over the complete range of soils and effluents employed.

Based on these observations, with correction for difference in soil temperatures existing between the laboratory and field, sustained BOD loadings of 200 pounds per acre day on soils of 15 to 20 inches in depth could be expected to result in percolates of high quality, unimpaired growth of selected cover vegetation, and no reduction in soil permeability due to BOD loading. Employing loading parameters of 27,000 gallons per acre day and 200 pounds BOD per acre day, high degree BOD removal could be expected for effluents with an initial concentration of 875 ppm. Since most effluents exhibit BOD concentrations less than this, it appears that permissible hydraulic loading will hold organic loadings below the critical levels in most instances. There are certain cases, however, where organic loading would be a design parameter.

In these investigations emphasis was placed on determining the organic loading limits which could be tolerated in land disposal operations without a substantial reduction in percolation rate or serious harm to the cover crop. While it was observed that defined loading limits do exist if these two conditions are not substantially altered, an excessive organic loading did not preclude a substantial BOD reduction during the time the effluent percolated through the soil. For example, BOD reductions of 55 to 70 per cent were common even when septic conditions existed in the substrate.

BOD reductions of this magnitude under anaerobic conditions led to an investigation of the degree of treatment afforded effluents percolating through the soil under simulated lagoons or seepage ponds.

In Figure 3 is a plot of BOD removal versus seepage rate and effluent residence time in the soil observed during the study. The effluents used were unbleached kraft and diluted kraft black liquor with a BOD in the 100 to 200 ppm range. BOD reductions were calculated from the difference in concentration at the soil surface and after percolation through the soil.

The BOD removal-seepage rate and BOD removal-soil residence time relationships shown exist for the

soil depth of 20 inches employed in the experimental setup. Soil residence time of the effluent is the most significant parameter of evaluation and a unit readily calculated for field installations from known soil depths and volume of voids data available in handbooks or established in the laboratory.

The BOD removals observed are as high as 80 per cent at a soil residence time of 27 days plus. As residence time declines, the BOD removal declines to about 20 per cent at a soil residence time of 1.7 days. Where 2-foot depth of soil is present, soil residence time at most field installations will be on the order of 10 days or greater since seepage rates of greater than 1 inch per day are uncommon. The high BOD removal afforded under these anaerobic conditions is undoubtedly due to the low loading rates employed. At a seepage rate of 5 inches per day, the BOD loading was 7.5 lb/1000 ft³/day, or about 1/10 that noted to result in BOD reduction of 60 per cent or greater in conventional laboratory anaerobic digestion of pulp mill effluents.

COLOUR REMOVAL BY THE SOIL

While it has been observed that BOD removal from effluents by the soil during irrigation is independent of soil or effluent type over the range investigated, the same is not true for colour removal when these effluents are applied as irrigants. Colour removal varies both with effluent type and soil type. A summary of some of the more significant observations is shown in Table 2, where colour reduction is expressed on a percentage basis for an irrigation period of 9 or 10 months. Where bleached kraft and insulating boardmill effluents, both with initial colour concentrations greater than 1000 ppm, were applied to the clay loam soils, 99 per cent colour removal was noted, while sandy loam removed only 65 per cent of the colour. It was generally observed that for all the kraft and insulating boardmill effluents employed the clay loams were most effective in retaining the colour, followed in effectiveness by silt loam and sandy loam in this order. Extensive colour intensification, averaging about 100 per cent net colour increase, was consistently

observed when both ammonia and calcium base sulphite effluents were applied to silt and sand loam, despite the fact that 35 to 90 per cent of the lignin present in the effluent remained in the soil during the period of effluent application. This increase was probably due to transformation of the lignin complex while percolating through the soil, resulting in a significant change in the light absorption capacity of the effluent. This phenomena may explain the apparent persistence of colour in ground water where contamination with sulphite effluents has occurred.

When appreciable colour passage was noted during the period of effluent application, leaching normally resulted in continued colour passage. When the applied effluent colour was above 1000 ppm or where sulphite effluents were applied, the leaching percolates from all except finely divided high cation exchange capacity Olympic clay loam soil exhibited substantial increases in colour content.

While it appears that the Olympic clay loam soil was capable of functioning as both a colour remover and colour retainer, the variability observed in the laboratory investigations dictates that proposed land disposal operations incorporate studies employing both the effluent to be applied and soil available at the site if ground water contamination might be detrimental.

The percolates from soil columns receiving effluents do not differ significantly in odour from that percolate from columns irrigated with tap water, both exhibiting the earthy odour of highly treated secondary effluents.

BIOLOGICAL QUALITY OF PERCOLATES

The percolates from columns to which kraft recovery condensates, sulphite effluent, and unbleached kraft linerboard mill effluent had been applied as irrigants were bioassayed using the guppy as a test specimen. There were no mortalities nor were distress symptoms noted during a 96-hour exposure period to 100

per cent concentrations of these percolates. This indicates that immediate discharge of percolates into a water course would have no effect on the aquatic habitat if the high degree of aerobic treatment provided by percolation through approximately 2 feet of soil is maintained.

CHANGES IN SOIL CHARACTERISTICS

Research and field experience have shown that certain water quality standards should be met where crop irrigation is practiced to permit satisfactory plant growth and to prevent undesirable physio-chemical changes in soil structure which may also interfere with growth.

While plants are directly affected by high total water salinity, adverse effects in the soil are directly related to the sodium content rather than total salinity. The most common method for expressing sodium level is the SAR or sodium adsorption ratio, defined as the ratio of sodium concentration to the square root of the mean concentration of calcium and magnesium. Depending on total salinity, waters are considered safe for irrigation and low in sodium hazard when the SAR ranges from 4 to 9. The basis of concern for sodium rests in the fact that both clay and humus particles in the soil act as ion exchange materials. When water of high sodium content is passed through the soil the adsorbed calcium and magnesium are replaced. This may cause a dispersion of the soil since both calcium and magnesium exert a flocculating effect due to the greater ionic charge. Increased dispersion may result in decreased permeability to both air and water.

Analyses of total kraft mill effluents have shown mean SAR values of 4.6 for bleached and 7.5 for unbleached mill effluents. This and correspondingly low salinity values indicate their potential as suitable irrigants.

In the laboratory investigations it has generally been observed that effluents with a SAR of 8 or less do not

create an adverse soil reaction. In fact, by judicious selection of a salt tolerant cover vegetation and permeable soil it has been possible to exceed the proposed classification limits for low sodium hazard without harm.

Exceptions to these observations have been noted, however. When high clay content soils previously irrigated with medium salt level effluents were leached with low salt content water to simulate the purging accomplished by natural rainfall a reduction in soil permeability was noted.

Since a substantial amount of information is available in the field of soil science dealing with the handling of conventional irrigation waters similar in salt content to those of many pulp mill effluents the relationship of the soil-salt-water reaction was established for soils irrigated with a kraft effluent and a synthetic effluent of like salt content.

Four soils--two clay loams, silt loam, and a sandy loam--were used as test series. Bleached kraft mill waste and a simulated effluent of like sodium, calcium, magnesium, potassium, sulphate, carbonate, and chloride content were applied as irrigants. These salts constituted the bulk of those present in the effluent and those of primary significance in soil management. The irrigants differed only in that one contained organic matter, the principal component of concern being lignin.

One means chosen to check response of a soil to the two irrigants was salt concentration in the percolate during the period of irrigation and subsequent leaching. Figure 4 is a plot of sodium concentration in the percolate versus inches of effluent applied for one soil. It can be observed that the concentrations were very similar for both effluents.

A striking similarity in concentration of calcium, magnesium, and potassium was also noted in the percolates as illustrated in Figure 5. Similar observations were made for chloride and sulphate levels.

The distribution of the predominant cations and ions in the percolates from four soils is shown in Table 3, where the weight difference is expressed as a percentage using the kraft effluent as a base. It can be observed that, with the exception of an apparent retention of calcium in two of the soils and some loss of sulphate in all soils receiving bleached kraft effluent, there are no significant trends indicated. The tendency for increased calcium retention in the presence of kraft effluent can be interpreted as a favorable response. Soil analyses tended to confirm these findings, as is illustrated in Figure 6 where total and water soluble sodium concentrations in a soil irrigated with bleached kraft and simulated effluent are shown at different periods during the irrigation season. An insignificant difference in total sodium content of the soils was observed to exist and only on one occasion was there a significant difference in water soluble sodium level. Other cation concentration levels in the substrate indicated that the four soils responded almost identically to the two effluents.

Despite the similarity of soil and percolate quality, the phenomenon of soil deflocculation consistently occurred in Olympic clay loam soil irrigated with kraft effluent when the salt concentration of the irrigant was radically changed, as occurred when leaching was started. This phenomenon was isolated to a single soil characterized by a high clay content and correspondingly high cation exchange capacity. This study did show, however, that in most cases conventional irrigation water use knowledge is applicable for disposal of pulp mill effluents and evaluation of potential application can be accomplished through known and commonly practiced analytical techniques.

Other parameters used to evaluate changes in soil characteristics due to effluent application were changes in soil permeability and cover crop condition. Reductions in soil permeability were associated with both excessive sodium loads and BOD loads in excess of 235 pounds per acre per day. These experiences have been previously described. Favourable experience with highly coloured effluents, such as caustic extract

wash water with an initial colour over 8000 ppm, and successful application for 18 weeks of 1/30 dilutions of kraft black liquor with a colour over 10,000 ppm and a lignin concentration 40 times that of bleached kraft effluent, indicated that the build-up of colour bodies in the soil is probably not significant in reducing soil permeability at field installations.

SOIL AMENDMENTS

Amendments to correct soil deflocculation attributed to sodium adsorption in the field of agriculture are similar to those employed in other fields where ion exchange is employed. Either calcium, sulphur, or both, are used with gypsum being the dominant source of calcium for replacement of sodium in the soil-ion exchange complex.

Gypsum and calcium hydroxide were both used to evaluate the effectiveness of soil amendments in the laboratory. This study was confined to Olympic clay loam soil previously irrigated with kraft effluent which exhibited definite indications of deflocculation and reduced permeability.

A calcium dosage suggested for use in actual field practice and predicated on the exchangeable sodium content of the soil was used for the study. The addition of the equivalent of 3 to 5 tons of gypsum per acre resulted in an increase in percolation rate from 0.3 inch per day to about 1 inch per day when cover vegetation was present. Two tons of gypsum, or an equivalent calcium dose in the form of calcium hydroxide, increased the percolation rate from 0.1 inch to 1 inch per day when cover vegetation was not present. In both cases response was rapid and independent of the source of calcium, indicating that conventional soil amendment practices are applicable should deflocculation be likely to occur when effluents are used as irrigants.

THE ROLE OF COVER VEGETATION

With the exception of delayed grass kill where sulphite pulp and papermill effluent was used as an irrigant, impaired grass growth has been accounted for by excessive organic loading or violation of well accepted soil and crop management practices. Examples of such violations are: high hydrogen ion concentrations in the irrigant creating acidic soils, excessive hydraulic loadings, or the use of irrigants with unfavorable sodium adsorption ratios. Within these limitations, however, the effluents employed have been observed to produce grass equally as well or better than tap water.

One of the more significant observations of the investigations has been the merit of establishing, and the need for adoption of, land disposal practices to maintain cover vegetation. Where maximum hydraulic loadings are desired, hence minimum land requirements such as is usually the case in waste disposal, the cover crop plays an important role. This was demonstrated by a twenty-fold increase in percolation rate on dense silt loam soil when a cover crop with an extensive root system was employed. Conversely, reduced percolation rates were consistently observed when conditions resulted in impairment or death of the cover crop during the irrigation season.

The alternate route of transfer for liquid afforded by evapotranspiration, and observed to lay between 50 to 90 per cent in the laboratory during the summer months, reduces dependence on percolation as the sole source of water removal from the upper soil strata. Prevention of classification and dispersion of soil at the surface, which impedes filtration, are added benefits of the cover crop. It appears highly doubtful at the present time that the most economical land use for irrigation disposal can be accomplished unless the program is tailored around suitable cover vegetation.

GUIDES TO FIELD APPLICATION

The laboratory studies employing soil as a media for treatment of mill effluents have covered a wide spectra. From these investigations a base for establishing general parameters for field application of land disposal has been derived and are shown in Table 4. These guides are predicated on the protection of cover vegetation whose root system provides substantial increases in percolation rate in dense soil while the leaf system provides a means for additional water consumption by evapotranspiration. Hence, corresponding reductions in land requirements for this method of treatment can be provided. Integration of a waste treatment program with a productive agricultural program holds considerable promise. In the laboratory investigations the grass yield from seed germinated and irrigated for a period of almost three years with unbleached kraft effluent is equal to that irrigated with tap water. Grass yields at least equal to those obtained from conventional irrigation water have also been noted for grass irrigated with other pulp mill effluents.

The BOD loading criteria of 200 lb/acre day are those observed under sustained loading, which did not cause a reduction in soil permeability or cause damage to cover vegetation, yet yielded in excess of 95 per cent BOD reduction as effluent percolated through 20 inches of soil. In most cases effluents up to 875 ppm BOD can be disposed by irrigation without exceeding the BOD loading criteria set forth.

The transport of colour through the soil was observed to vary during the period of irrigation depending both on type of soil and effluent applied. In general, it can be said that sandy soils passed the colour while clays and loam held most of the colour bodies during the irrigation season. The major exception was noted with sulphite effluent where colour intensification of the drainings was commonly noted. The practice of land disposal, therefore, is not without potential ground water contamination problems which must be evaluated for individual situations.

The control of hydrogen ion concentration is dictated by good soil and crop management practices. Irrigation water in the range of 6.5 to 9.0 pH units is suitable for most crops and soils. Laboratory studies have revealed that there is no difference in grass growth rate nor were any other signs of harm noted when kraft effluent at pH 9.5 was used as an irrigant for a period of 12 months. High residual carbonate content of some soils may permit the use of effluents lower than pH 6.5

The laboratory experience indicates that effluents with a SAR of eight or less can be satisfactorily used as irrigants on most soils. Exceptions have been noted with the clay soils, however, and substantially lower SAR values are indicated if soil deflocculation is to be avoided.

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TABLE 1

EFFECT OF BOD LOADING ON PERCOLATE QUALITY,
COVER VEGETATION AND SOIL PERMEABILITY

BOD Loading Lb/Acre Day	BOD Reduction Percent	Cover Vegetation Condition	Soil Permeability
280	60-84	Poor	Impaired
< 235	95+	Good	Satisfactory

TABLE 2

EFFECT ON SOIL TYPE ON COLOUR TRANSPORT

Soil Type	Effluent	Applied Effluent Colour ppm	Colour Reduction Percent
<u>During Effluent Application</u>			
Clay loams	Kraft and insulating board	1000+	99
Sandy loam	Kraft and insulating board	1000+	65
Silt loam and sandy loam	Sulphite	500	(-) 70
Soil Type	Applied Effluent ppm	Percolate Colour Change	
<u>During Leaching</u>			
Olympic clay loam	1000+	Negligible	
Other soils	1000+ or sulphite	Increase	

TABLE 3

DISTRIBUTION OF CATIONS AND ANIONS IN THE PERCOLATE DURING IRRIGATION WITH
BLEACHED KRAFT AND SIMULATED EFFLUENT OF LIKE SALT CONTENT

Mg Added in Effluent		Soil Type	Mg Found in Percolate		Weight in S	Difference Simulated %
			BK	Simulated		
Na	880	Olympic Clay	665	712	+	7.1
		Sandy Loam	820	829	+	1.1
		Red Aiken Clay	780	838	+	7.5
		Silt Loam	810	844	+	4.2
Ca	76	Olympic Clay	113	120	+	6.2
		Sandy Loam	137	169	+	13.4
		Red Aiken Clay	73	76	+	4.1
		Silt Loam	126	196	+	55.5
Mg	15	Olympic Clay	133	133		0
		Sandy Loam	137	169	+	1.1
		Red Aiken Clay	113	120	+	6.2
		Silt Loam	123	126	+	0.6
K	22	Olympic Clay	67	67		0
		Sandy Loam	31	37	+	9.4
		Red Aiken Clay	23	28	+	1.7
		Silt Loam	123	136	+	5.2
Cl	1610	Olympic Clay	1470	1650	+	2.2
		Sandy Loam	1500	1627	+	8.5
		Red Aiken Clay	1565	1598	+	2.1
		Silt Loam	1528	1622	+	6.2
SO ₄	259	Olympic Clay	276	249	-	9.8
		Sandy Loam	233	268	-	6.8
		Red Aiken Clay	180	146	-	8.9
		Silt Loam	332	272	-	8.1

TABLE 4

Guides and Considerations in Field Application
of Land Disposal of Pulpmill Effluents
Based on Laboratory Investigations

BOD	< 200 lb/acre day
Colour	Individual site investigation
pH	6.5 - 9.0
SAR	< 8 on permeable soils

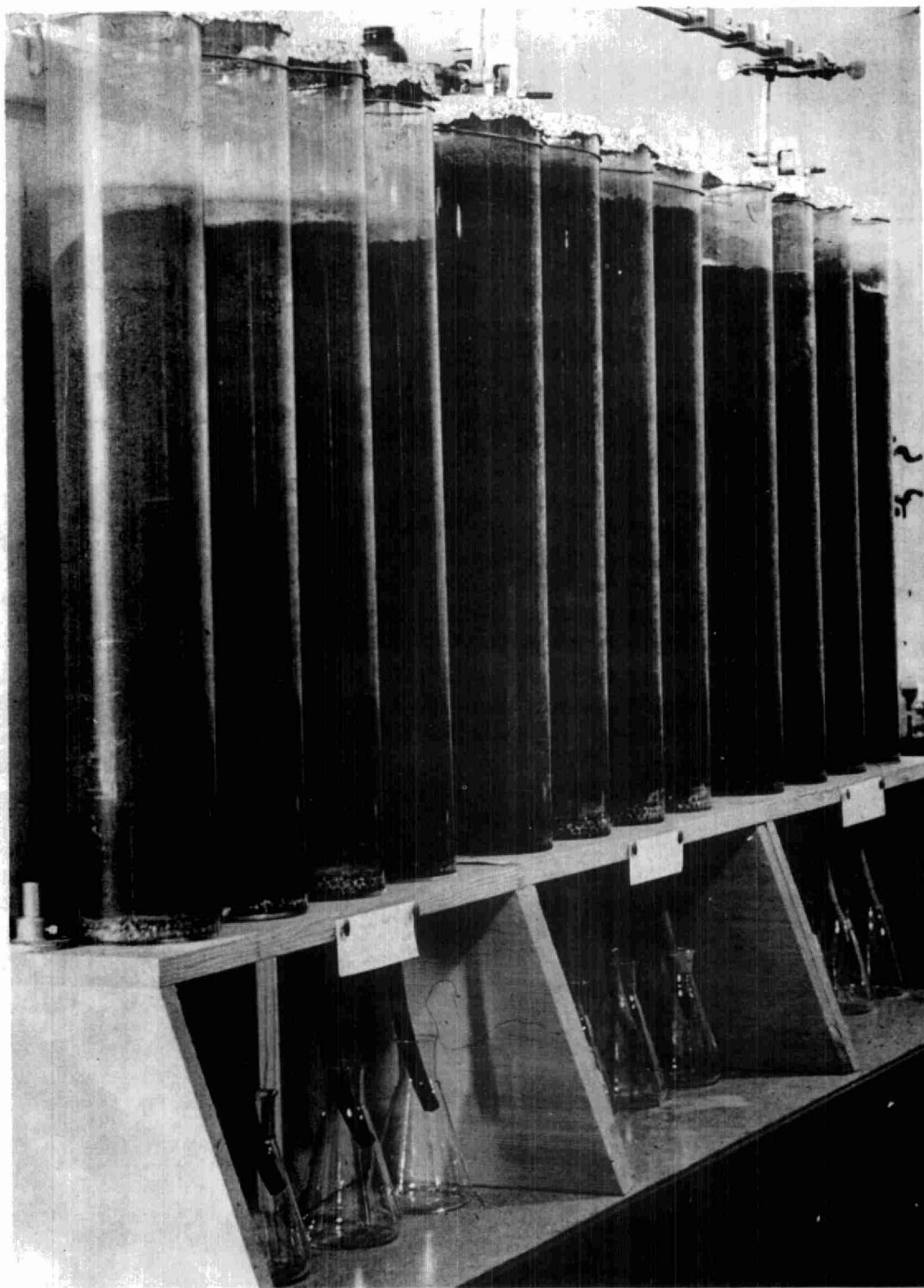


FIGURE 1



FIGURE 2

Figure 3.
BOD Reduction During Percolation Through
the Soil Under Simulated Seepage Beds

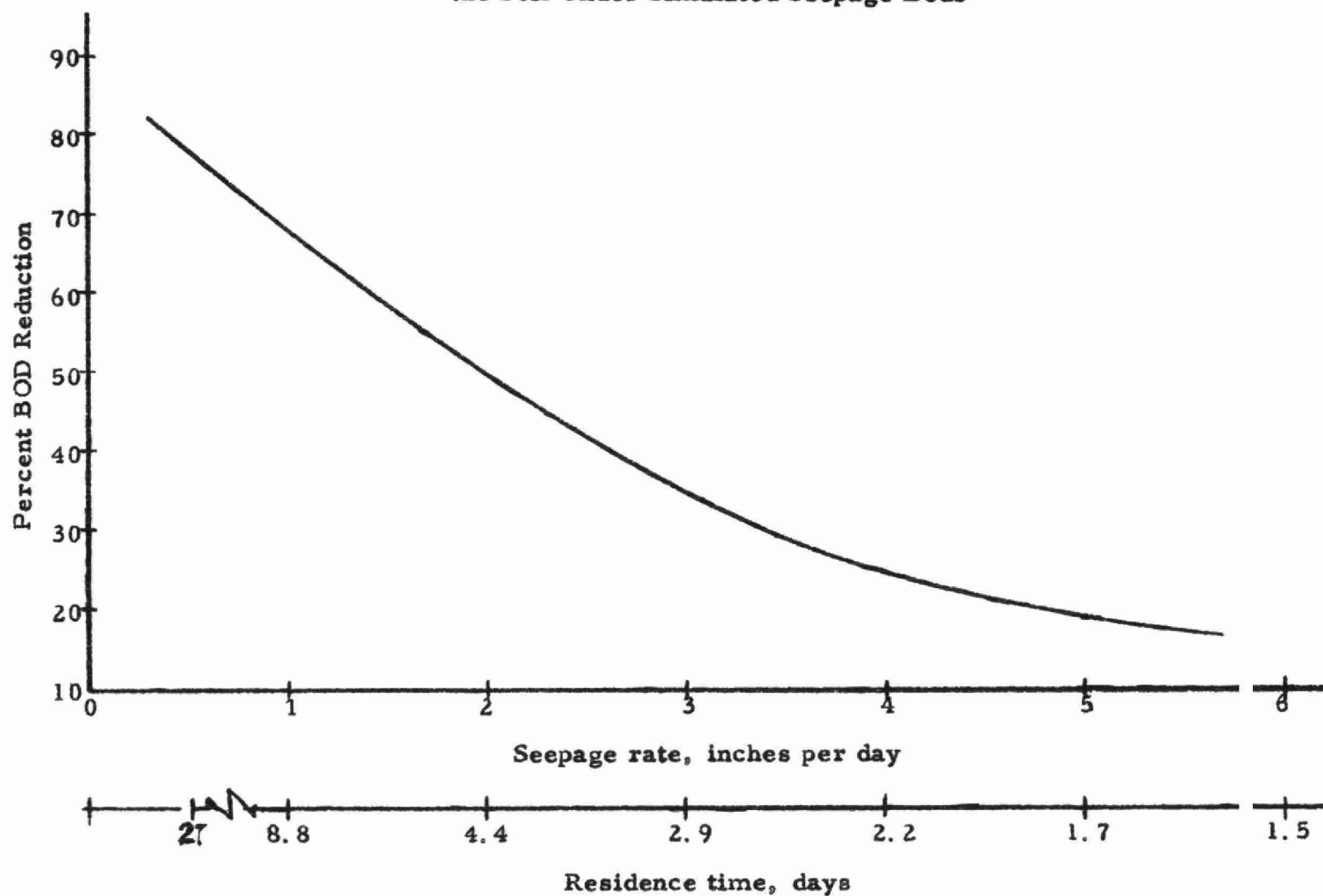
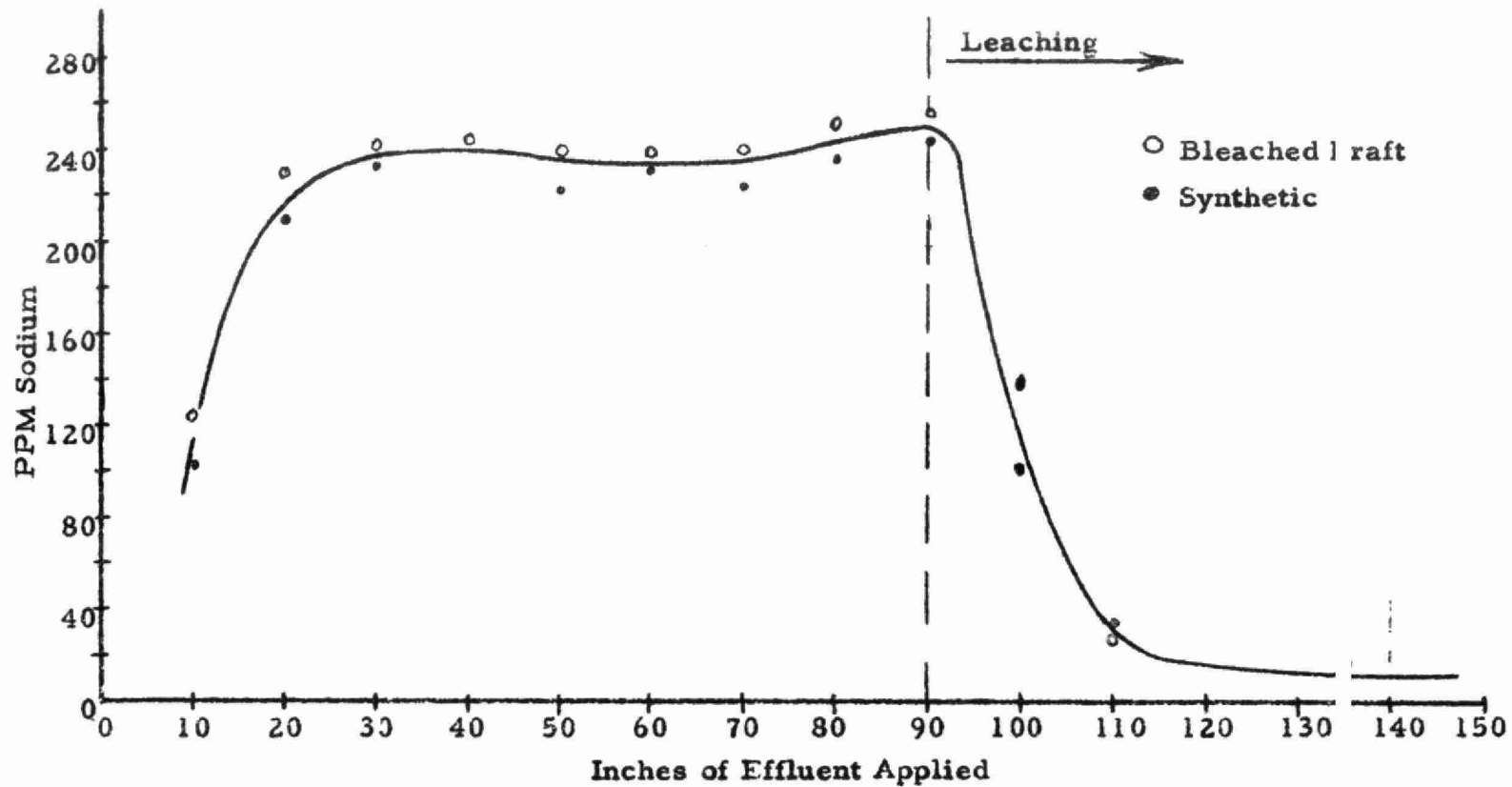


Figure 4.

Sodium in Percolate from Clay Loam Soil
Irrigated with Bleached Kraft Effluent and Synthetic
Effluent of Like Salt Concentration



NCSI - 1963

Figure 5.

Cations in Percolate from Clay Loam Soil
Irrigated with Bleached Kraft and Synthetic
Effluent of Like Salt Concentration

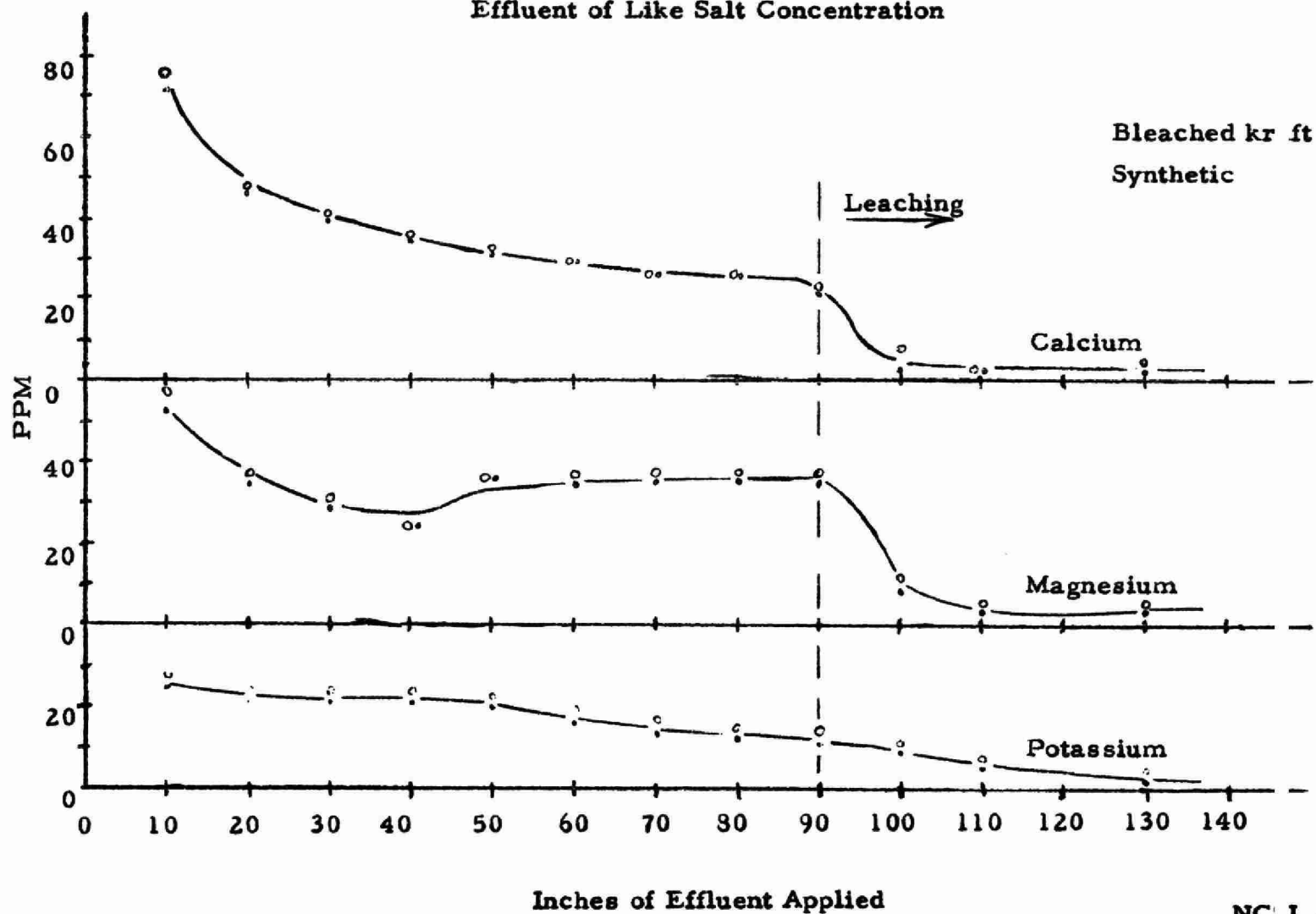
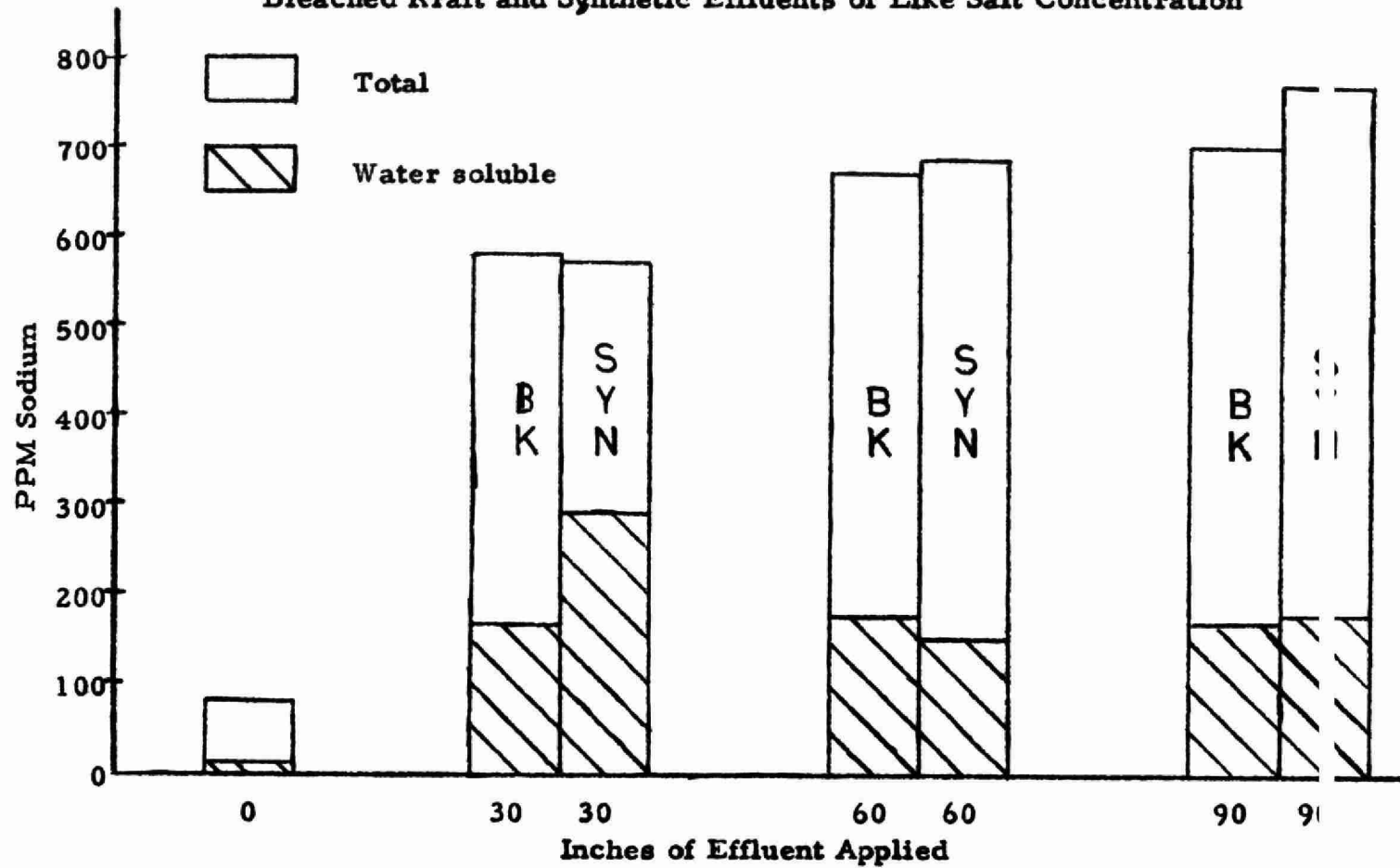


Figure 6.

Sodium Accumulation in Clay Loam Soil Irrigated with
Bleached Kraft and Synthetic Effluents of Like Salt Concentration





BANQUET ADDRESS

"CANADA, THE AWKWARD ADOLESCENT"

by

PROFESSOR MARCUS LONG

Mr. Chairman,

It was very nice of you to provide me with such a distinguished and well-prepared audience and, at the same time, to insist that I must not talk about industrial waste or polluted waters.

Perhaps I should talk to you about women. Unfortunately I am not an expert on this subject.

(After telling a few stories to relax the audience and demonstrate what women can do for and to men Professor Long then announced that he was going to talk about Canada.)

It is almost forty years since I left Ireland to seek my fortune in Canada. In these forty years I have learned to love this country. That does not mean that I have ceased to love Ireland. No one can ever really forget the place of his childhood.

Ireland is a small country: It could be lost in Lake Superior. The Creator had to work there like a miniature artist. Those who have seen His work will appreciate His skill.

No one who has seen them can ever forget the blue-hazed mountains of Mourne, the soft rolling hills of the Glens of Antrim, the rugged coast of Connemara

where the bubbling streams rush noisily down the cliffs to lose themselves in the raging foam of the frustrated Atlantic, the soft pasture lands of Meath or the oft-sung beauties of the Lakes of Killarney.

In Canada the Creator had a larger canvas and stroked with a larger brush. The results are magnificent. This is a land of great sweeping rivers, seemingly endless forests, majestic mountains and broad prairies. It fills the observer with awe and a sense of his own littleness.

It is depressing to think that so many men and women in both countries are not worthy of their natural heritage. One is inclined to recall the lines of a famous hymn;

Where every prospect pleases
And only man is vile.

Beautiful Ireland is a land of prejudice. Protestants and Catholics hate each other for political and religious reasons. In the City of Belfast no Protestant can live on a Catholic street and no Catholic can live on a Protestant street. Gentle men and women sometimes become killers in the name of God.

I still recall my sense of pride in Canada when I found that in this country Protestants and Catholics could live on the same street, belong to the same political party and work together. The escape from the depressing atmosphere of prejudice was like a breath of fresh air.

I soon found that Canadians had their own prejudices expressed in a mutual intolerance between French and English-speaking Canadians and that the promise of Canada was illusory.

It was a sad discovery that Canadians, who ought to know better, act like so many of the worst elements of humanity. This business of mutual hatred is a universal phenomenon. Hindus and Muslims kill each other in the name of religion, the Flemish and the Walloons tear Belgium apart, the Greeks and the Turks strike at each other's throats in Cyprus.

There is no sense to it. No one was ever born a Hindu or a Muslim, a Protestant or Catholic, Greek or Turk. We are all born as human beings into certain cultural patterns. It is the home and the school and the church that make us Protestant or Catholic, Greek or Turk. Education can be a powerful instrument of propaganda, the source of prejudice.

The struggle in Cyprus has no foreseeable peaceful solution because the Greeks want to be Greeks and the Turks want to be Turks and nobody wants to be a Cypriote. The tensions increase in Canada because so many of the French want to be French and so many of the English want to be English and so few want to be Canadians.

Perhaps it is an historical misfortune that the English and the French have claims of priority in settling the fate of this country. In a whimsical mood I suggest it might be better if the problem were taken out of their hands and given to the Irish and the Scottish.

The Scottish and the Irish are as proud of their ancient cultures as the most loyal of the English and the French. I hope no one will misunderstand if I remind the English and the French that Ireland was a land of saints and scholars when their ancestors were barbarians.

Yet we have not come to this country to impose our culture on anyone. We come not to conquer but to contribute.

I remind you that when the Irish and the Scottish came to this country they refused to let religion, language or colour of skin interfere with their love-making. Almost all second-generation Canadians carry some Irish or Scottish blood in their veins.

This is true of such distinguished French Canadians as our Governor-general and the former Prime Minister, Louis St. Laurent. The famous hockey player

Boucher, we are told, had an Irish mother who spoke French better than his French father. And we salute that most French of French-Canadians, Father O'Neill. I don't mention Daniel Johnson since he is not Irish!

Several years ago I was asked to speak about Canada at a reception for visiting teachers from other parts of the Commonwealth. I chose as the title of my address, Canada, a Child among Nations. If I were given the same opportunity today I should change the title to read, Canada, The Awkward Adolescent, for the truth is that so many of us are acting like bewildered teenagers.

The typical teenager, I remind you, wants to be master of his own house and yet cannot break away from his old home; he is sure he knows better than his elders but his decisions are usually more emotional than rational; he is on the verge of maturity but often acts like a child. The picture seems to fit us.

Schizophrenia, insofar as it reflects a split-personality, is a most tragic form of mental disorder. It used to be called Dementia Praecox, the mania of adolescence. Canada is an awkward adolescent.

It is good policy when faced with adolescent disturbances to look for their roots in a troubled childhood. We may find the sources of our troubles in our history.

Canada had an unfortunate early life. This country was born by accident. The original discoverers were not looking for this land but for a passage to the Far East. The unwanted child was then neglected. French-Canadians know this. They know that their ancestors in Canada were abandoned. The English forget that they were treated as badly. At one time the British government was prepared to take Guadaloupe rather than Canada as the prize of war. We are told that though they approached the passage of the British North America Act with apathy many Englishmen were relieved to be freed so easily from the political and financial embarrassment of Canada.

Canada was unwanted and treated as a foundling by both parents. As a result, this country was peopled largely by losers. The French of the Plains of Abraham were joined by the Loyalists who chose the wrong side in the American revolution.

It is a wonder, with such a history, that the country survived at all.

The pressure of time makes it impossible to expand on the points I have made nor would I want to do so if I could. I suggest that too much attention to its history is one of the curses of Canada.

Please do not misunderstand me. No one should, even if he could, forget his past. You can no more cancel the past than you can cancel yesterday. Yesterday is the fertile ground out of which today was born. You are what you are because you were what you were.

Nor would I condemn anyone, either English or French, for loving his past. I merely point out that there is a vital difference between loving the past and wanting to live in it. The desire to return to the womb, the disorder known as infantile regression, is what I want to avoid. Canada belongs to the future rather than to the past.

I am as proud of being Irish as anyone is of being English or French or anything else but I refuse to be called an Irish-Canadian. The hyphen would suggest that while I am here in body my interests and my love are elsewhere. That is not true. For good or ill my lot is cast with Canada. I hope that some day when the census-taker comes to call on my children they will be able to declare, for census purposes, that their father was a Canadian!

The past should not be forgotten nor should anyone easily and without good reason surrender his cultural heritage. That I take for granted. But the past is something to build on, not to live in. Those who are prisoners of the past can neither meet the

challenges of the present nor the opportunities of the future. That is why I deplore the fact that so many of the French in this country want to be French and so many of the English in this country want to be English. How much better if all of us sincerely desired to be Canadian.

It is not possible to spell out, on an occasion such as this, what it means to be a Canadian. I am not sure that anyone can. Yet the general direction is clear. We are asked to co-operate in the building of a nation rooted in French and English culture and enriched by a variety of other cultures. We must resist any attempt to make the French English or the English French and work to remove any injustices that would make either group feel that it has been betrayed. At the same time we, who are neither English nor French, must resist any attempt to make us anything but Canadian. Since we represent more than one-third of the population this does not seem to be an unreasonable demand.

This is hardly the time to raise the question of a distinctive Canadian flag but the question can hardly be avoided since the controversy about it is a mark of the distemper of this country.

I sympathize with those who insist that the Union Jack must be retained in some form. The Union Jack has always been to me a reminder of the British struggle against tyranny and a mark of the evolution of British judicial and political institutions that have contributed so much to our modern freedom. If a flag, containing the Union Jack, were acceptable to all the citizens of Canada I should be happy. But it cannot be. The Union Jack is a reminder to French-Canadians of their betrayal by France and their defeat by the British. I could not support any flag that would be a source of irritation to one-third of our people. I want a flag that all Canadians may accept.

It is no easy task to build a nation out of the variety of peoples we have in this country, particularly when the two major groups, who falsely

think of themselves as different races, are more anxious to preserve the past than to build the future. But it is not a Canadian trait to be discouraged by obstacles.

The first travellers through Northern Ontario must have been appalled at this wilderness, a country fitted only for savages and wild beasts. Yet Northern Ontario became the main source of our mineral wealth at the beginning of the century. The first travellers from Lake Ontario to Lake Erie must have cursed Niagara Falls as a damnable obstacle to the progress of honest men. Yet Niagara Falls, when harnessed, became the source of the power that turned South-western Ontario into a rich industrial centre.

There is a moral in this for all of us. It seems to imply that men can only be defeated when they defeat themselves. The early travellers, I suspect, retreated; the problems of the wilderness and the Falls were too great for them. The visionaries, calling on intelligence, learned how to use the obstacles of nature for the benefit of mankind.

You are concerned with the problems of water pollution, among other things. You are quite aware that simple solutions to your problems are either not available or likely to be misleading. And yet you are confident that you can find solutions. I ask only that you give a part of that spirit, that faith in intelligence, to the problem of Canada.

Canada is a wonderful dream. I hope we won't turn it into a nightmare because we are more in love with the past than with the present, with emotion than with reason, with divisions rather than unity.

Canada must not be either French or English. It must be both and more. We who are neither English nor French want to be a significant part of this promising nation, neither dominating nor being dominated.

We know about prejudice and the hatred that can be bred in religious and political differences. We want no part of them in this new land.

We know about injustice and our hearts are set against it. Show us wrongs against others and we will work to undo them.

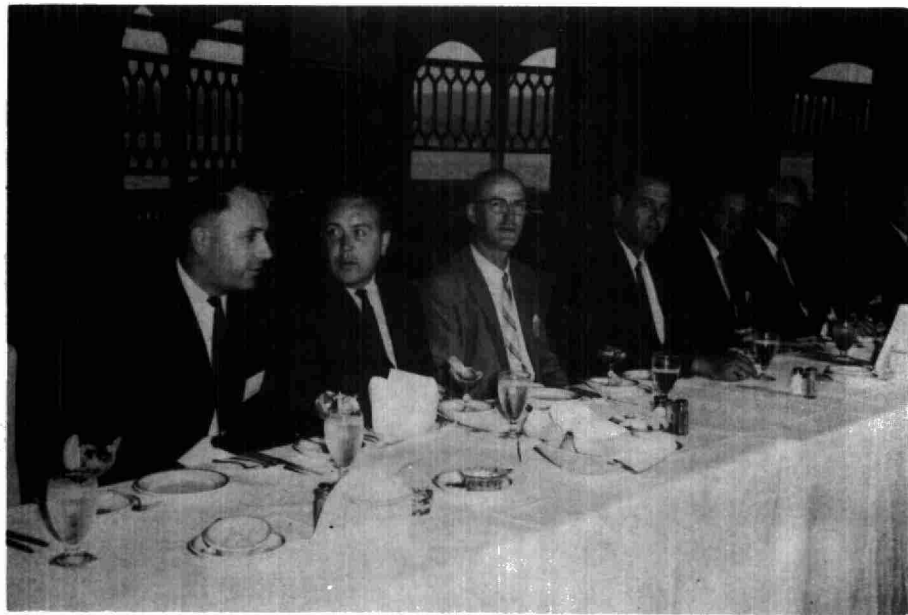
We are captured by the vision of a Canada in which people of various ethnic and cultural origins can work together for the common good.

Canada is, in miniature, what we would like to see the whole world become. Canada is a country in which people from different cultural backgrounds can live in harmony, each respecting the views of others without surrendering his own and yet aware that a new country requires new attitudes and that a slavish adherence to the past is no way to tackle the future.

If we cannot solve the problem of Canada we cannot solve the problem of the world.

There go all our beautiful dreams. We shall leave to our children a country divided by prejudice and a world tottering on the brink of war. There is no sense in it.

Canada is not so much a nation as an opportunity and a dream. I urge you to work to make the dream come true.

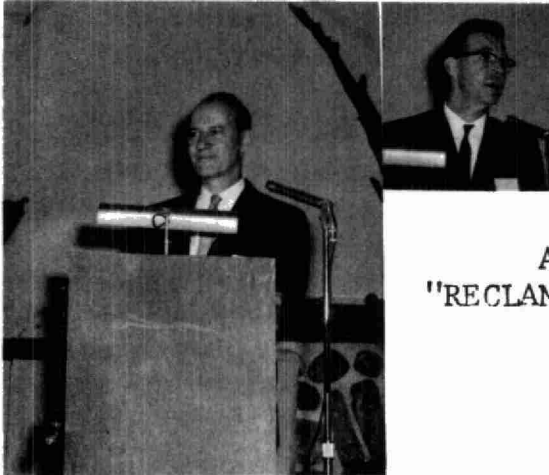


HEAD TABLE



HEAD TABLE

SESSION FIVE



R. A. Johnston
Ontario Agricultural College
Department of Microbiology
Session Chariman

AN INTRODUCTION TO
"RECLAMATION OF PROCESS WATER"

by

W. J. MILLER

A paper was presented at the Canadian Pulp and Paper Association convention held in Montreal in January of this year which had as its title the "Reclamation of Process Water", the author being my colleague David J. Randall, process engineer at N. B. International Paper Company at Dalhousie, N. B.

Since process water in the pulp and paper industry contains characteristics that cause pollution, any reclamation should inevitably bring with it a reduction in pollution, and for this reason this paper, it is hoped, will be of interest to this conference.

Firstly, let me indicate that I do not intend to read the paper in detail. I would like to make a few remarks of a general nature relative to the particular situation at Dalhousie and to the position of the pulp and paper industry as a whole.

In years past the pulp and paper industry located itself on the fringe of the vast timber lands of Canada where wood and water were in unlimited Supply. As the industry prospered and expanded, so

did the rest of Canadian economy and population. This introduced competitive demands for water, both in quality and quantity, which has placed this "grandfather industry" in a position with special problems of its own with regard to waste disposal - recalling Mr. Blosser's paper of yesterday as an example.

The concern of the author of this paper is with reclamation, not primarily pollution. The immediate purpose for reclamation was the expansion of the Dalhousie mill beyond the capacity of the adjacent drainage basin to store sufficient water to ensure continuous operations at an augmented production rate. This region has a mean annual precipitation of 40" but, as with all averages, a low of 27" for the year 1960 was nearly disastrous. We now know that with production rates in a trade where 5 to 10 year contracts are normal, we cannot be dependent on the whims of nature and it was necessary to adopt measures to obtain a greater margin of safety.

If I might digress for a moment, it is almost axiomatic in the pulp and paper trade that the higher the quality or grade of product, the more water per ton is required. While this is in a sense true, particularly of the paper pulp and dissolving grades, the newsprint grades have also been traditionally users of best quality water in unlimited supply.

Compared to some of the quantities of discharges mentioned in papers over the past few days, the influents and effluents of paper mills are themselves virtually large rivers.

When I first came in contact with this aspect of the work several years ago, I sought out the assistance of Hugh McFarlane when I found it almost impossible to make a reasonable material balance between "water taken in" and "effluent out". He comforted me with the thought that very often water just seemed to be pumped into a mill and disappears through "invisible" holes in the floor. I have since found that the maze of sewers of some of the older mills puts the sewers of Paris to shame.

(Mr Miller then abstracted from the original paper by D. J. Randall which is entirely reproduced below.)

"RECLAMATION OF PROCESS WATER" BY D. J. RANDALL

Water is an extremely important raw material in the manufacture of newsprint. In some locations its availability is taken for granted and water literally passes through the mill. In the Dalhousie mill of the New Brunswick International Paper Company water is a precious commodity because it is an uncontrollable quantity subject to the whims of nature. As a result reclamation has been used extensively to reduce the amount of fresh water make-up required and at present amounts to 40 per cent of the total water consumed.

The following paper will describe briefly the nature of these reclamation installations as well as some of the background details of the fresh water supply itself.

It should be noted here that although white water reclamation and the use of salt water is also extensive, it will not be covered in the following test.

The source of fresh water for the Dalhousie Mill is the watershed of the North Branch of the Charlo River. The drainage area is approximately 90 square miles and during average rainfall the river flow is approximately 10 million cu. ft. per day.

The concrete dam, which forms the reservoir is approximately 350 ft. wide and stands 85 ft. above the floor of the ravine through which the North Charlo flows.

The centre line of the pipe intake is at elevation 140. Between elevation 145 (minimum) and 168 (top of dam) the dam holds back about 71 million cu. ft. With the addition of 32-in. flashboards this capacity has been increased to 83 million cu. ft. An additional 31 million cu. ft. is stored below elevation 145 but pumping facilities are necessary to use this water.

The pipeline from the dam to the mill is a 32-in. i.d. wood-stave pipe of 1-5/8-in. B. C. fir. It is 44,992 feet long (8.52 miles) with about 32,860 feet of it above ground (73 per cent).

The pipeline capacity is 1500 cfm with water in the dam reservoir at 168 feet. A decrease in this level results in a corresponding decrease in flow to the mill. The required flow at the mill is approximately 1300 cfm.

The water enters the mill through a cast-iron pipe and is collected in a fresh water pond after passing through inclined wires to remove debris. The pond has an approximate capacity of 84,000 U. S. gallons. A venturi flow meter is used to record the volume entering the mill.

The difference in flow between what is possible and what is required at the mill does not leave a very wide margin of safety. The two factors affecting flow through the line are freeze-ups or icing and lowering of the head in the Charlo dam reservoir.

One of the first major freeze-ups occurred in January 1950. The conditions which appeared to have allowed the formation of ice in the pipeline were freezing rain and lack of snow cover on the pipeline (75 per cent above ground). We were able to thaw out the line by using three steam boilers and a bulldozer to cover the line with snow.

In January 1958, a survey was made of the conditions conducive to the formation of ice in the pipeline. It was found that although outside temperature, wind velocity and ground temperature contributed, the inlet water temperature and snow cover were the major factors. The pipeline should be safe at temperatures down to -30 deg. F. and winds of up to 30 mph provided the pipeline is adequately covered with snow and the inlet temperature of the water remains above 33.5 deg. F. (corresponding to 35 deg. F. at the mill).

We have now installed a permanent steam boiler with a capacity of 10,000 lb. per hr. to be used when the water temperature or flow decreases to the danger level.

The second factor affecting capacity in the pipeline is a lowering of head at the dam. As explained earlier the minimum head is at elevation 145. The minimum head to maintain flow is at 168. With flash boards on and adequate flow into the reservoir there is sufficient head, but with light precipitation during the summer and fall or a late break-up in the spring the water level can drop dangerously low. The last serious drop occurred in the summer and fall of 1960 and the spring of 1961. The low in 1960 was 158.9 and in 1961, 150.3.

Besides conserving water at the mill, the reservoir can be augmented by pumping from a lake upstream into the Charlo River. This lake, Popelogan, is located about 26 miles upstream from the dam and about 1500 ft. over a ridge from the Charlo River. It has a potential capacity estimated at 57 million cu. ft. (Reservoir 83.5).

In 1960 using a 14 x 12 pump the lake was used from September 13 to October 26 to supply approximately 230,000,000 U. S. gallons to the Charlo River system. We were able in this way to maintain the water level until the rains came near the end of October. The year 1960 was one of the driest on record totalling 27.54 in. for the whole year compared to an average of 40 in. in other years since 1933. It is interesting to note that this year to the end of July we have received almost 40 in. of precipitation.

Since everyone talks about the weather but no one can do anything about it, we were required to look for some other way to ensure sufficient water to run the mill.

The original supply was based on a 400 tons per day mill using about 2.16 million cu. ft. per day or 1500 cfm. An increase in production since then to 850 tons per day has meant an increase in the demand for process water.

The two main approaches to the problem were increased storage capacity above the dam and reclamation of mill process water.

The latter approach has been the one used to date.

The 1947-48 major changes were made to the sulphite system. One addition was a 138,000 U. S. gallon wood stave surge tank. This tank was used to collect reclaimed water for use in the sulphite mill. The main source of reclaimed water the seal water for the paper machine Nash vacuum pumps amounting to about 1750 U. S. gpm and cooling water from the Emman's gas coolers in the digester building. An automatic valve controlled by the tank level was used to supply the necessary fresh water make-up.

Since then changes have been made to the machine room Nash pump recovery system so that the total reclaimed water is approximately 3800 U. S. gpm.

This system reclaims from the following sources:

	<u>U. S. gpm</u>
1. Nash pumps: 12H12, 5L11, 2L9	3000
2. The water used in the deculator vacuum systems of No. 2, 3 and 4 p.m.	500
3. Miscellaneous, including press pits, water removed at presses, press showers, etc.	300

This water is passed over an inclined wire before entering the surge tanks to remove extraneous material.

In 1951 a system was installed to reclaim cooling water from the turbo generator room coolers and condensers and later from the Jenssen gas coolers in the acid plant. The estimated recovery from this system is 700 U. S. gpm. This water is normally returned to the fresh water pond but can be pumped directly to the sulphite surge tank through the automatic valve previously mentioned.

In 1958 a sump was installed to recover 150 to 300 U. S. gpm from the primary transformer cooling system. This water is used in the groundwood mill headbox to the high pressure pumps.

In 1961 a system was installed to reclaim water used in the grinders in the groundwood mill for the operating stands and bearings. This is estimated at 50 U. S. gpm per grinder line or about 800 U. S. gpm. This water is pumped to the fresh-water pond. Plastic piping was used on this job but was subsequently changed to s.s. in places where it was necessary to pass the pipe through the grinder pits.

In 1956 investigations were made into the use of a water clarifier for recovering stock and water from mill sewer effluents (paper mill and wrapper machine basement). In 1957 a Waco filter supplied by Sherbrooke Machineries Limited was installed. This is a travelling mat type unit with a capacity of 2000 U. S. gpm of clarified water of about 0.002 per cent consistency. This water runs by gravity to the sulphite surge tank.

The latest addition to our recovery system has been the reclaiming of water used in the sulphite regulator vacuum system. Again this is reclaimed to the surge tank.

In addition to these reclaiming systems we also collect water from the machines reel drums, sweat dryers, press and couch bearings and compressor after-coolers in a separate tank. This water is then used as hot water showers on the paper machine deckles, presser roll showers and press internal showers.

It may be added that we have made fairly extensive use of the flow recorders on the fresh water supplied to the process and recovered through reclamation. These along with a fresh-water pond level recorder and a surge tank level recorder enable us to trouble shoot more easily during critical periods of water shortages. The fresh water pond supply line from the Charlo Dam can also be put under automatic control to reduce losses due to overflow at the pond when the water level at the dam is low.

In summary it may be said that fresh water supply is a major problem in the production of newsprint at Dalhousie. With the present facilities we are limited to a maximum of about 11,250 U. S. gpm or approximately 2540 cu. ft. per ton. The remaining water must come from reclamation. The present system has a reclaim capacity of approximately 7500 U. S. gpm or 40 per cent of the total water used.

This has been a brief description of the fresh water system used at the Dalhousie Mill. Technical data have been omitted so the various reclamation sources and not the particular methods employed would be emphasized.

ACKNOWLEDGEMENT

Paper presented at the Annual Meeting of the Technical Section, Canadian Pulp and Paper Association, Montreal, January 28-31, 1964; reproduced by permission.



"CO-OPERATIVE APPROACH TO
SOLVING DIFFICULT
INDUSTRIAL WASTE PROBLEMS"

by

C. E. COOLEY

Many papers have been presented by representatives of Federal and State governmental agencies concerning specific authorities vested in various water pollution control laws, and the impact of such laws on their "targets," these "targets" being industries or municipalities discharging wastes to public waters, particularly those having no treatment or inadequate treatment of their wastes for the protection of the receiving public waters.

It is not my intention to elaborate on these laws, nor on their advantages or disadvantages. However, I do think it is important to discuss briefly the background of the Virginia Water (Pollution) Control Law and philosophy of the Virginia Water Control Board and its staff in order for you to better understand our approach to the overall problem of industrial waste pollution control.

After World War II, the increased demand for more and better consumer goods brought about tremendous changes in our industrial community. Those industries producing war goods had to re-tool their plants for producing consumer goods or the raw materials for these goods. During World War II, water pollution had been forgotten in favour of concentrating all efforts on fighting and winning a war. As a result, water quality

degradation had by war's end assumed significant proportions, and most governmental bodies, Virginia among them, recognized the need for adequate control legislation.

In 1946, the Virginia State Water (Pollution) Control Law was passed. This law is administered by the Water Control Board (hereafter referred to as the Board), consisting of five members appointed by the Governor.

In enacting the Law, the Virginia legislators assumed that reasonable amounts of impurities from man's wastes may be discharged to water courses, consistent with their many other uses, such as public and industrial water supplies, recreation, shellfish, fishing, agricultural and other uses.

Under the law, the Board has the authority to (1) determine which of the many--and at times conflicting--uses of streams should, in the public interest, be protected, (2) specify the water quality (standard) that it determines is necessary in streams consistent with such uses, (3) require municipalities and industries that discharge wastes to modify these wastes appropriately, by treatment or other means, so that the water quality objectives will be attained and (4) monitor and police the streams under its jurisdiction in connection with enforcing the water quality objectives that have been set.

Experience has shown that the Virginia Law is basically strong enough to accomplish the foregoing objectives. It must be emphasized, however, that if a great majority of the industries and municipalities had not co-operatively and voluntarily proceeded to abate and prevent pollution of State waters, the Board's work would have been infinitely more difficult and, in many instances, progress would have been at a virtual snail's pace.

We must recognize the need to control and manage the quality of our public waters and that we all share the legal and moral responsibility to maintain

these waters for the greatest possible public benefit. This means that there must be communication, co-ordination, and co-operation between regulatory bodies, industry, political subdivisions, researchers and educators, the public and others, some of whom may be only remotely aware of the problems involved. There must be a dissemination of facts and ideas so that we can all pull together toward a common goal--cleaner streams for all. If we do not adopt and maintain this attitude, we will probably have a greater need for legal experts in the field of water pollution control than for engineers and scientists.

In Virginia, as elsewhere, we recognize the need for industrial growth, and having a number of groups actively engaged in industrial development, we know that this calls for even closer management of our public waters, so that the quality may be maintained for all possible interests. This can be accomplished only through the sincere and co-operative efforts of all the groups involved, to obtain the information on the basis of which the Board may make sound and just water quality decisions.

There is general agreement as to the design criteria applying to processes and process units for the treatment of municipal wastes, but this is not true for the treatment of industrial wastes, since each industrial waste has its own peculiar characteristics.

The receiving body of water itself should be the first and last consideration in determining which (of the sometimes many) impurities need to be removed from a particular industrial waste. For example, it is obvious that a waste discharged to a stream having a 10-year drought flow of 100 cfs used for fishing and recreation requires a much higher degree of treatment than the same volume of waste discharged to one having a 10-year drought flow of 1000 cfs and the same uses. After considering the waste to be discharged in relation to the requirements of the receiving body of water, the solution may be relatively simple. Then again, depending on the nature of the waste, there may be no solution at all.

While the details of the actual working procedures followed by the Board and its staff have not been discussed in this paper, I believe it is important to emphasize that we attempt to operate on an informal basis whenever possible. This approach has been a valuable and effective tool in Virginia, as it has been in other states, for making progress in pollution abatement. In this approach, the polluter voluntarily assumes his responsibility and formulates, with the regulatory agency, a mutually acceptable water quality improvement program that will be of greatest overall benefit. In a spirit of mutual good faith, it permits work to be done and methods tried without having to cross the "t" and dot the "i". It leaves the formalities to the last, as a matter of administrative necessity. It also leaves the regulatory agency free to invoke formal enforcement in the relatively few cases where polluters either will not voluntarily make corrections, or where the regulatory agency thinks progress is too slow.

Many and varied problems are encountered by the water pollution control agency in an effort to carry out its responsibility and yet to make reasonable decisions relating to management of quality of the public waters within its jurisdiction. This applies particularly to industrial wastes, where, as pointed out earlier, each industry constitutes an individual and separate problem. The following examples will give you some idea of the types of industrial waste problems which we have encountered and the approach that was taken in each in an attempt to work out a satisfactory solution.

SEVERAL STATE AGENCIES AND AN OWNER CO-OPERATE TO EFFECT A SOLUTION

The Board was recently faced with the problem of deciding whether a duck farming industry could continue discharging wastes to a very large tidal river, which is used for both oyster production and recreation. It seemed apparent that the industry could treat its waste and maintain water quality for recreation. However, chemical treatment of the waste

for maintaining water quality consistent with the harvesting of oysters for direct marketing appeared to be economically inconsistent with the industry's continued operation. Yet, the continued discharge of the untreated waste seemed just as economically unjustified for the oyster producers, because there was a possibility of permanent restrictions on several hundred acres of adjacent public oyster grounds.

Soon after this problem came before the Board, its staff began accumulating information by literature search, correspondence, and by visiting several duck farms on Long Island. We found few sources available to give us the information we needed. However, we knew that the wastes contained the following substances which could possibly degrade water quality in the receiving stream:

1. Sludge-forming solids,
2. Organic material having a BOD,
3. Coliform bacteria,
4. Nutrient constituents,
5. Odor, and
6. Color or turbidity-producing substances.

Based on the characteristics of the receiving waters, the only constituents that we considered to be of any significance were the solids and coliform organisms.

This owner has a unique duck farming operation, in that it is completely self-contained. He has (1) brood ducks for laying eggs, (2) incubator facilities for hatching the eggs, (3) facilities for raising the ducks to a 5-7 pound marketable bird in 8 weeks, (4) facilities for mixing and grinding all of the feed, (5) slaughtering and packing plant facilities, and (6) freezer capacity for storing the processed birds. There is essentially no waste from the processing of the ducks since there is a market for the feathers, viscera, and feet, which would normally be waste materials.

The waste is generated solely in the raising of the ducks. At the age of approximately 2 weeks, the ducks are moved from the brooder houses to outside pens and spend the rest of their short lives moving from pen to pen until, at the end of 8 weeks, they finish up at the processing plant. During this time the ducks have full access to a flowing stream of water, where the waste is generated. Analysis of the waste has shown that coliform organisms may range up to 10,000,000 organisms/100 ml, and settleable solids may be as high as 25 ml/l.

In our search we learned that the solids could readily be kept out of the stream by simple settling. From our experience with treatment of municipal sewage by lagooning or ponding, we felt that we could effect a substantial coliform reduction in the case of this waste by this method. Laboratory-scale experiments confirmed our opinions.

The Board held two hearings, at which much testimony, pro and con, was offered, and after considering all pertinent information, it directed:

1. The owner, in order to obtain as much water quality improvement as possible ...to construct...primary settling basins followed by lagoons of sufficient capacity for 4 days retention* of the wastes, and
2. The staff to co-operate with the State department of Health, Virginia Polytechnic Institute School of Agriculture and Extension Service, Virginia Institute of Marine Science, and the owner on a study of the wastes to obtain the necessary data on which it could base...final action.

* The 4 day retention was based on the previously mentioned laboratory-scale studies by the staff, which showed 99% of the solids would be removed in the settling basin and approximately 90% of the coliform organisms.

In accordance with the Board's directive, there was formed a committee composed of representatives from the above mentioned organizations, and a program was outlined for the proposed study. In the meantime, the owner proceeded with construction of lagoons having the required retention time. Subsequently, one of the Board's trailer laboratories was moved to the site and a technician was employed to analyze samples taken at various points in the treatment system to determine its effectiveness for coliform reductions, as well as samples from the receiving public waters.

In discussing the significance of the coliform organisms, it should be pointed out that the United States coliform standard for waters from which shellfish may be taken for direct marketing is a median value of 70 most probable number per 100 ml. Based on the data obtained from approximately 50 stream sampling stations during this study, the State Department of Health removed restrictions from approximately 400 acres of productive public "rocks" (grounds), which means that approximately 90% of these "rocks" can now be utilized for direct marketing of shellfish. The remainder of the public "rocks" are in shallow water and are not particularly productive.

The duck farm owner controls all but approximately 40 acres of the privately leased shellfish grounds. It might be pointed out that regardless of the degree of treatment, restrictions would remain on those oyster beds within a radius of approximately 1/2 mile of both discharges.

For recreational uses, there is no generally accepted standard of bacterial quality, but values ranging from 500 to 2500 mpn of coliform organisms per 100 ml have been used in other states. The committee considered only those values below 500/100 ml to be satisfactory for recreational purposes. After installation of treatment facilities at both farms, the river was considered to have a bacteriological quality satisfactory for recreational purposes at all stations except in the immediate vicinity of the treated discharges.

Therefore, in its report to the Board the Technical Committee stated:

"that treatment facilities installed by the owner will protect approximately 90% of the public productive shellfish beds and result in recreational quality water in the receiving body of water, except the area in the immediate vicinity of the two discharges...(but) that continued maintenance of water quality satisfactory for recreational uses and shellfish production will depend on diligent operation of the treatment facilities. Of particular importance is the removal of solids from the waste prior to lagooning."

SEVERAL OWNERS AND A REGULATORY AGENCY
CO-OPERATE TO SOLVE A PROBLEM

In Virginia we have four menhaden fish processing plants, which are all located on the same small land-locked tidal estuary. These plants, of necessity, must be located at a navigable sea-coast port for convenience of the fishing boats, and originally, to permit easy disposal of waste materials to coastal waters.

These plants were constructed long before the Water Control Law was adopted and direct "over-board" disposal of the wastes was common practice and construction of the plant on pilings over the water made it extremely convenient to do so. For this reason, a later program of pollution abatement proved very complex and difficult. Besides mechanical difficulties, because of plant layout and location, pollution abatement was further complicated because the process wastes have an extremely high BOD some of which range from 100,000 to 175,000 mg/l.

There are a number of powerful potential pollutants generated in the operation involved from the unloading of the fish to shipment of the final products.

1. To unload the fish boats at the plants, it is necessary to "wash-down" the fish; that is, the fish are made water-borne and pumped from the holds of the boats by a specially designed pump. Since this water tends to get "heavy" because of the flesh particles, scales, oil and blood, it is desirable to use only clear water in unloading processes. Prior to the Water Control Law, this "once-through" use of clear water and discharges of the contaminated wash water to the creek was practiced at all the plants. They now re-use this contaminated water and store it for later transfer to a boat which disposes of it some distance off shore, where it does not create any problems.

2. The fish are then passed through rotary screens for de-watering before being counted volumetrically. The liquid is returned to wash water storage. Waste carry-out by drag-lines and drippage from other mechanical equipment, makes this point in the process a prime source of contamination.

3. After counting, the fish are stored in "raw-boxes". Most of these "raw-boxes" are constructed of wood planking on pilings over the water, and originally all leakage went to the creek. This waste is similar to the wash water waste above.

4. From the "raw-box" the fish are moved by drag-lines to a steam pressure cooker, after which they are moved by screw conveyor through a press, where the liquid portion is extracted. Here stream contamination may occur from spillage and leakage of the press liquor.

5. The solid portion, or fish meal, is then dried in direct-or-steam-heated rotary driers. After drying, the meal is ground and sold as fertilizer supplement, or as a supplement for various animal feeds, mainly poultry.

6. The press liquor is then centrifuged for removal of suspended solids and oil. The oil is stored for sale after further treatment, and the remaining water-base reject liquid, referred to as "stickwater," is transferred to storage tanks for later evaporation and reclamation of solids. Previously, this stickwater was, for the most part, discharged to the creek. Even with the current practice of evaporation it is still a potential source of contamination.

It should be apparent from the above brief description that pollution abatement at these plants is difficult, at best, and in the early 1950's the plants retained consultants to determine the best method for handling the wastes from these plants. The consultants found that it was impractical to chemically treat the wastes since very little BOD would be removed, and a sludge handling problem would be created that could not be successfully solved. The consultants concluded that the only practical way to abate pollution from the plants would be to intercept the wastes before discharge, mix them with the stickwater and evaporate the mixture.

Accordingly, each of the four plants made changes to convey all wastes through central collection systems to their stickwater storage tanks for evaporation. This was done by "bottling-up" wastes using retaining walls around tanks and equipment and drip pans under pumps, wooden raw boxes and other units.

These changes resulted in a great improvement of the creek, but the plant operators soon became relaxed in their attitude toward pollution abatement,

and the creek began to slide back to its previously degraded condition. Unfortunately, the Board's staff was not sufficiently large to carry on the policing action which was indicated.

Prior to the 1960 fishing season, in an attempt to reach some general solution to this problem, the staff and representatives of each of the four plants met to discuss the overall situation. The group concluded that, in order to have effective control of waste discharges, constant inspection of the plants for leaks and spills was necessary. Since the Board's staff was too small to spare any permanent employees for this purpose, the plant owners and the Board agreed to participate in underwriting the cost of hiring additional men, with the understanding that the Board would have complete control of the inspection program.

Each summer since 1960 we have employed two men for round-the-clock inspection of the plants and creek and in only one of those years, 1962, did we experience significant degradation of water quality. On the basis of the 1962 plant inspection reports and conditions in the creek, the Board felt it had no choice but to institute legal action against three of the four plants, seeking to enjoin them from making further unauthorized waste discharges. In essence, the plants paid for the evidence which convicted them. However, the suits did not come to trial because the plant owners were able to convince the Board, by their change in attitude and by making certain improvements at their plants, that the situation was corrected and would not recur. Since the Board was only interested in the end result, and since it felt that conditions had improved, the pending suits were withdrawn. Even after this action, the owners were still willing to continue the program as in the previous seasons.

We feel that over the years we have attained a mutual understanding which has led to a very agreeable and workable co-operative venture and we now have a closer working relationship with the owners than was ever thought possible.

POLICING BY THE REGULATORY
AGENCY SOLVES A PROBLEM

The coal mining industry in Virginia dates back to the early part of this century and is concentrated in several counties in the Appalachian region of Southwest Virginia. Because of its small staff, located in Richmond, 300-odd miles away, the Board found it difficult to maintain an adequate water quality management program in the Southwest. Consequently, it has only been in recent years that the Board has been able to make a concentrated effort towards improving water quality in the coal mining area.

Because of the demand for clean coal, a large percentage of the coal mined in Virginia is washed and graded in preparation plants before shipment. The plants are all located adjacent to streams which may carry contamination into adjacent states. The plants are of necessity located at these points because the stream valleys provide the only level ground available and because this is where rail facilities are located.

After the coal is brought from the mine to the surface, it is transferred, usually by conveyor belt, directly to the preparation plant or, if the plant is located some distance from the mine, it is necessary to transfer the coal from mine cars to trucks or rail cars for shipment to the plant. The coal is then washed and the refuse material, made up of shale or slate, is conveyed to storage bins for later transfer to a refuse disposal area. The coal is screened and graded according to size, and is either stockpiled or loaded directly on rail cars for shipment.

The wash water contains several hundred mg/l of coal and rock particles which are very readily settled in a basin having several hour's retention. After settling, the water can be discharged with no noticeable effect on the quality of the receiving stream. It was formerly common plant

practice to discharge the wash water directly to the streams without benefit of settling. This caused serious stream discoloration, as well as deposition of tons of coal and other fine particles in the stream beds.

One of the first important steps the Board took in its attempt to improve water quality conditions in Southwest Virginia was to amend all existing certificates issued to coal preparation plants to include a provision stating that the waste water discharged to receiving State waters from the plants would not have more than 2 ml/l settleable solids, and that it must not cause discoloration. Although this was a sound and reasonable way to approach the problem, closer surveillance over these industries by the Board's staff was necessary, which at the time was almost impossible because of a small staff and other equally pressing problems throughout the state.

It appeared that the coal plant operators were not willing to work in mutual good faith, and during a recent summer period a part-time employee was stationed in the area. During his tenure, we obtained considerable evidence against several plants. The Board first issued each of the plants an order to cease and desist the discharge of this material to public waters. The owners did not choose to abide by these orders, so the Board referred the cases to its special legal counsel directing him to proceed with the necessary legal action. Injunctions were obtained in all but one instance, and that owner was placed on probation for a period of time.

The information obtained during this period was significant and pointed out the need for a full-time coal waste inspector. The Board thereupon authorized the establishment of a permanent position on its staff to carry out such an inspection program, and an inspector was employed. For the past year, this program has proved effective in maintaining very good water quality conditions in the area. Within the past year, the Board has filed suits against three more

companies for violating the provisions of their certificates, or for violating an order. Permanent injunctions were granted in two cases and the other is still pending.

Since this program began, there has been a marked change in the attitude of the plant owners and operators. The atmosphere is completely different than it was just a few months ago. Most of the owners are now recognizing their responsibility and accepting waste disposal as an ever-present operating problem.

Of course, some of the owners need to be reminded occasionally of their responsibilities, and our inspector is constantly pointing out locations around the plants where improvements can be made for greater water quality protection.

AN INDUSTRY ACTS VOLUNTARILY TO SOLVE A PROBLEM

There are some industries which accept their responsibility in water quality management without hesitance and take the initiative to solve their own problems.

A pulp and paper mill located in Southside Virginia, manufacturing bleached and unbleached paper board, assumed the initiative before passage of the Water Control Law, and began taking steps to protect a small tidal river which is used for recreation and fish spawning.

The company's first step was to make in-process improvements and experiments to treat a small portion of its total waste load by lagooning it. The experiment proved fruitful enough for the plant to install a lagoon having approximately 300 acres capacity. The larger portion of its waste was diverted to this lagoon for treatment and flow regulation during the fish spawning season. The owner also experimented with spray irrigation for treating some of the more concentrated wastes. The mill is now using spray irrigation for a small volume of its waste containing approximately 30% of the total BOD load.

The small river joins two other rivers at the state line downstream, and flows into that state. The downstream state stream quality standard calls for a minimum of 4.0 mg/l dissolved oxygen. This standard was not being met.

The company then undertook a concerted study of its problems to determine what should be done to insure that the water quality standards in the downstream state would be maintained. It adopted a plan to purchase approximately 2400 acres of land and constructed two additional lagoons, at a cost of approximately four million dollars.

The first of the new lagoons, of approximately 1640 acres, has a dike perimeter of 6-1/2 miles and a capacity of over 10 million gallons.

The effluent from the first new lagoon is discharged to the second new impoundment, which has an area of approximately 720 acres and a capacity of approximately one billion gallons, which permits regulated discharge to the receiving stream. At present mill capacity, the three ponds (approximately 2700 acres) will retain the entire effluent from the mill for about 480 days if required. This gives considerable flexibility in the operation of the waste treatment facilities during droughts.

It is interesting to note that the Board has never issued this company a formal directive or order indicating that it was dissatisfied with the company's progress towards improvement of water quality. To my knowledge the company has always voluntarily initiated action and approached the Board to present its plans and ideas for improvements.

The newly-constructed waste treatment facilities are the outcome of several years of serious planning and consideration. Had it not been for the company's attitude and initiative, I doubt that the present substantial water quality improvement would have been made.

PROBLEMS WITH NO SOLUTION

Theoretically there is a solution to every stream pollution problem, even if it means invoking the drastic step of closing the plant completely. We have such a case in Virginia.

This plant has been producing soda ash continuously since it started operating on July 4, 1895. It now also produces caustic soda, bicarbonate of soda, chlorine, dry ice, liquid carbon dioxide, fused alkalies and hydrazine. The damage to the river is caused by about 2 million gallons per day of waste water from these manufacturing operations, which contains in solution about a million pounds per day of calcium chloride and 500,000 pounds per day of sodium chloride, plus some settleable solids.

The wastes are treated in a settling basin where substantially all of the settleable solids do settle and are kept out of the river. Of course, the calcium and sodium chlorides in solution are not affected and they are discharged from the pond to the river.

Since it was organized on July 1, 1946, the State Water Control Board kept this problem under active consideration and has worked with the company over the years in an unsuccessful attempt to reach a satisfactory solution.

This company has a waste disposal problem that is different than that of any other industry in Virginia. Once the wastes have been produced there is no way to treat them to remove the polluting materials. By saying "there is no way to treat them" is meant that there is no known scientific technology for accomplishing this even if unlimited funds were available. We know of no chemicals that could be added to the wastes to destroy them. Neither do we know of any way that the polluting constituents in the wastes may be reduced by biological means.

The obvious answer, of course, would be to change the process or to modify it in some way to prevent formation of the polluting constituents in the first place. Under the conditions of operation and using the raw materials available at the location, there is no other known way, at this time, to produce the products that are manufactured.

In view of the above-mentioned facts, and after many technical conferences, Board meetings and hearings and after pondering the problem from every conceivable angle, the Board concluded in 1956 that shutting down the plant is the only possible way to permanently clean up the river to everyone's satisfaction. The Board reached this conclusion because science has not yet come up with any method by which the wastes may be treated or disposed of so that the river will at the same time be clean and usable for other purposes.

About the only positive action the Board could take, short of shutting down the plant, was to issue an order which requires that the discharge from the pond be regulated so the chloride concentration in the river at the point of discharge is maintained constantly at 5,000 parts per million or less. In other words, the peaks and valleys of chloride concentration that used to occur have been eliminated. This concentration of chloride is much too high, but is as low as it can be if the plant is to continue to operate.

In 1960 a downstream state, under Public Law 660, the Federal Water Pollution Control Act, requested the United States Department of Health, Education, and Welfare to intervene and take action against this operation. After three conferences, at which well-known scientists presented testimony on the treatment and disposal of this waste, the conclusions previously reached by the Virginia Board were confirmed, and the Federal government has taken no action.

This does not by any means imply that the matter has been closed. The company has installed a new pond, and flow from the impoundment areas is regulated, according to the Board's order, and

according to dilution volume available in the river, to maintain even concentrations of chloride at downstream points where water is used. However, research on this problem has failed, to date, to develop any new technology for treating or disposing of this waste so as to effect a real solution to the problem.

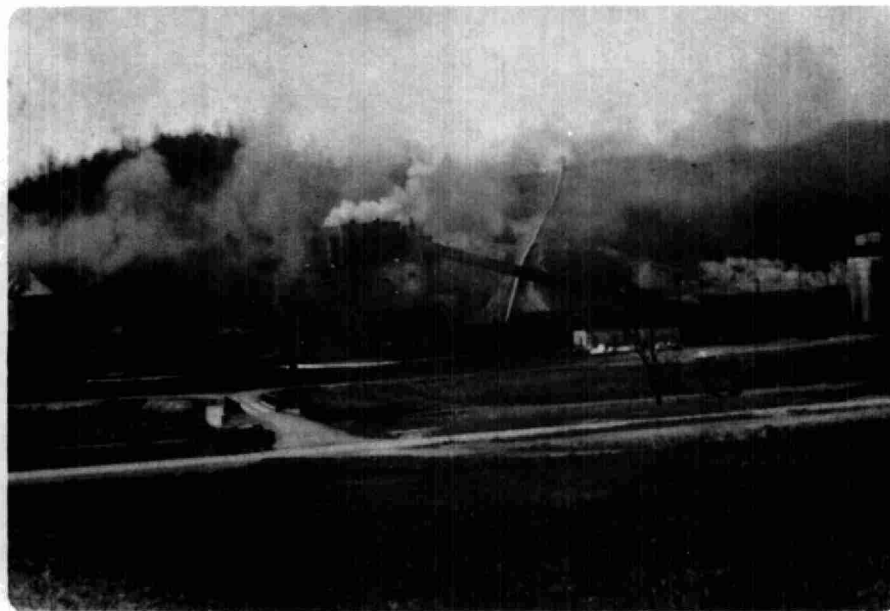
Briefly, the Board, under present technology, has only two choices in this matter. It may require (1) ponding of the wastes and regulation of the discharges to the stream, which the owner is presently doing, or (2) removal of the salt, which would in essence force the plant to shut down, an action which neither the Board nor the Federal government have felt justified in taking.

SUMMARY

To summarize, I believe it is important to stress that in order to obtain and maintain water quality for the benefit of all, the various factions involved in water quality management must be willing to co-operate, co-ordinate, and communicate.

It is gratifying to note that most industries today recognize and appreciate their responsibilities to maintain clean streams, and that they have made determined efforts toward reducing the impurities in their wastes to improve and protect stream water quality.

The general public is becoming more and more aware that there are clean stream programs, and as it demands better quality water, our problems will continue to mount. That being the case, none of us can sit back and rest on our laurels, because the future will place ever greater demands on everyone working in the field of water quality management. Therefore, it is imperative that we have a mutual understanding and respect for each other's problems. In this way only we can expect to obtain suitable water quality for the greatest possible benefit.



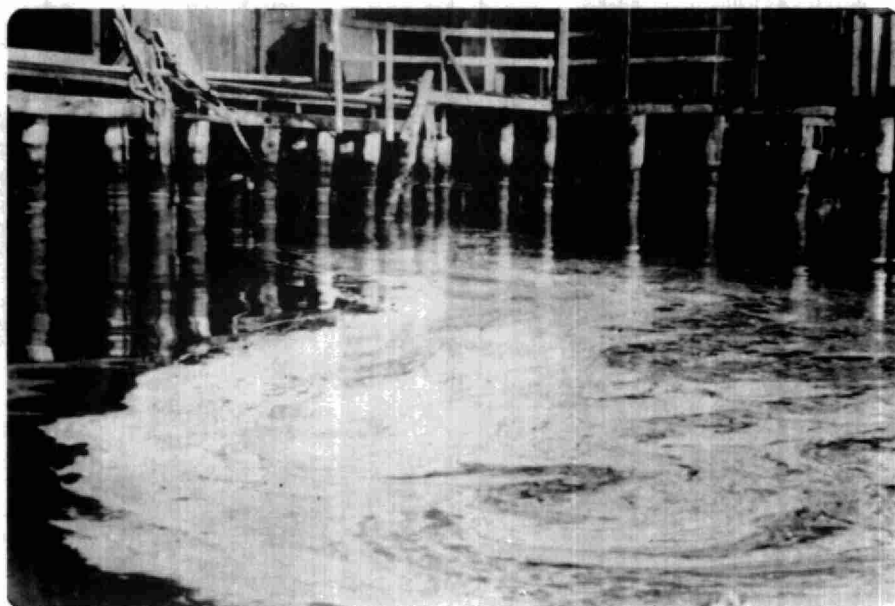
1. Typical Coal Preparation Plant in Southwest Virginia



2. Deposit in Stream Caused Coal Washer Waste



3. Menhaden Fish Processing Plants and Discoloration of Receiving Waters by Waste Discharge



4. Typical Conditions Around Menhaden Fish Processing Plants, Prior to Beginning of Surveillance Program



5. Raising of Ducks on Flowing Stream of Water
(Waste is Generated by Feed Material from
the Ducks)



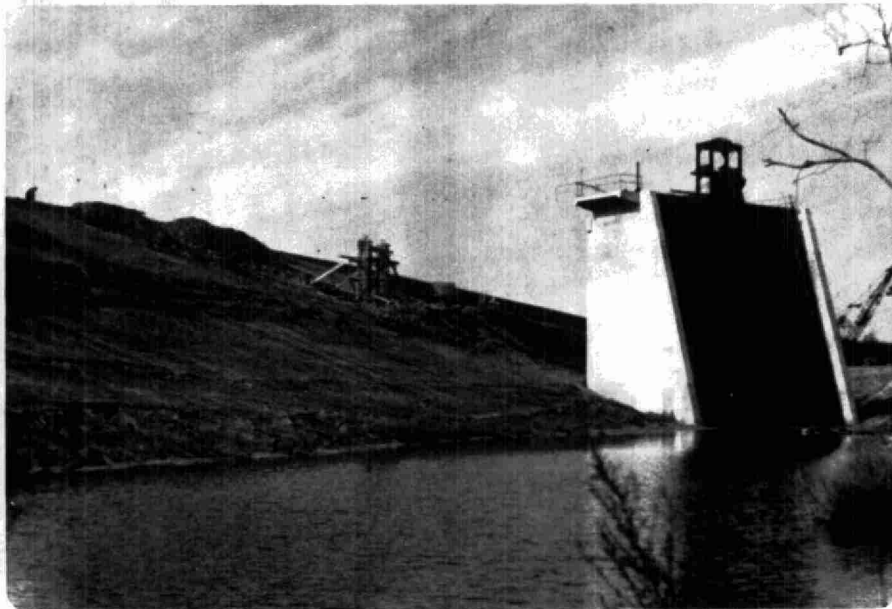
6. Duck Farming Operation Adjacent to Large
Tidal River



7. Lagoon System for Treating Wastes from Duck Raising Operation



8. Spray Irrigation of Waste from Large Pulp and Paper Mill



9. Effluent Discharge Structure Serving
Approximately 2700 Acres of Impoundment
Area Containing Bleached and Unbleached
Kraft Paper Waste



THE GOLF TOURNAMENT



"SOME CONFUSING ASPECTS
OF NEUTRALIZATION WITH LIME"

by

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ABSTRACT

Perhaps the most common contaminant of industrial waste streams is acid. A considerable amount of research has been done to devise economic means by which to treat such wastes, but there are still some confusing, if not conflicting, viewpoints in the pertinent literature. This paper will show that there exists a difference of opinion as to what are the simplest and self-evident facts concerning acid waste neutralization and will resolve these opinions, where possible, into clear statements and/or point out the necessity for more research.

Much has been written about lime and its use as a neutralizing agent. Most textbooks indicate how simple it is to design neutralization systems when lime is used. However, a thorough review of the pertinent literature could lead to some curious conclusions. For instance, the best neutralizing agent for acid wastes is caustic, or it is definitely limestone, but it is without a doubt soda ash if it isn't hydrated lime or quicklime. Quicklime, of course, must be slaked prior to use, but under some conditions it may only need to be pulverized. Limestone must be pulverized down to 200 mesh if it is to be used efficiently in split treatment plants, but using a bed of limestone

chips is the simplest way to treat waste acid. Dolomitic lime, with its higher available basicity, is readily slaked in 200°F. water, but you get most efficient neutralization by storing the slaked dolomitic paste for several hours and then lagooning the waste after treatment unless the lime was pressure hydrated. Hot water is, of course, necessary for efficient slaking of quicklime, but best slaking is accomplished in cold water for the particles of slaked lime should be very small to get faster neutralization reactions; however, the specific surface should be low so that subsequent precipitates will settle out faster.

A somewhat trite saying may be appropriate, and that is: "If you are not confused, you don't understand the situation."

Many of the previous statements are particularly unfunny to consulting engineers who have faced the task of designing acid waste treatment facilities. Engineers will collect, review, and digest all the pertinent information they can get their hands on before they, in this case, build a pilot plant.

There are many proposed and/or generally accepted methods for treating acid streams. They include: (a) mixing available acid and alkaline waste streams, (b) reclamation by ion exchange, dialysis, volatilization, spray-burning or indirect combustion, and (c) neutralization with limestone, caustic, soda ash and/or lime. This paper will deal with the chemical neutralization methods, concentrating mainly on neutralization with, if the pedantic will forgive the expression, lime. (ASTM Designation C51-47: "Lime - A general term which includes the various chemical and physical forms of quicklime, hydrated lime, and hydraulic lime used for any purpose.") We will show that there exists a difference of opinion as to what are the simplest and self-evident facts concerning acid waste neutralization. We will try to resolve these opinions, where possible, into clear statements or to point out where more research is required.

CAUSTIC SODA AND SODA ASH

There is wide agreement that caustic soda and soda ash are excellent neutralizing agents. The fundamental truisms are that they are comparatively expensive chemicals; their reaction with sulphuric acid (the most common component of acid waste streams) is rapid and produces a soluble salt; systems employing these chemicals are relatively easy to automate; their use will increase the dissolved solids; soda ash has been used to bring the pH of waste effluents up to around 6, and caustic to bring the pH of waste up to around 11. The design of treatment systems is made somewhat easier because these basic facts are well substantiated and clear. There are companies which can afford and do use soda ash and/or caustic for waste treatment.

LIMESTONE BEDS

An earlier review of the subject summarized the experience gained by using various types of limestone beds.¹ While successful applications of the upflow type beds have been reported², many problems are associated with the process. Problems are created by capsular coatings of calcium sulphate and hydrated iron and by carbon dioxide evolution. Alleviating these problems by dilution or by using dolomitic limestone just creates another set of problems. Dilution and/or the longer reaction times required by limestones containing magnesium carbonate (if they react at all) may indicate the need for larger units or recirculation. The recirculation must be sufficient to maintain a rate of application high enough to keep the bed expanded and to scour out the insoluble precipitates and yet low enough to avoid washout. With flow control, limestone feeders, balancing tanks, a clean and reactive limestone, and close supervision, this system will work and perhaps at a slightly lower chemical cost. The use of pulverized limestone will be considered in a subsequent section of this paper.

QUICKLIME

Most authors dealing with the subject of quicklime, hydrated lime, or lime slaking will point out that the product of even a computer-programmed calcining process will have a variety of chemical and physical properties. It is common practice to advise that most lime suppliers will explain what can happen during the calcining process and how this can determine the ultimate use of the lime. A few authors have offered some very interesting information on crystal structures and dispersion characteristics of quicklime and hydrated lime. Opinions on the significance of these physical characteristics may also be found in the literature.

With all this data available, it almost seems naive to ask if dolomitic lime truly has a higher available basicity. Does the magnesium oxide portion of dolomitic lime slake in non-pressurized slakers? Must it be slaked to neutralize acid wastes? Must high calcium lime be slaked? Should it be slaked in cold or hot water?

It is true that answers to these questions may be readily found in the literature. Several answers may be found, all slightly different.

Five years ago, R. J. Baker reported in his article entitled "Recent Developments in Lime Slaking"³ that "only the calcium oxide portion of dolomitic quicklime hydrates under normal hydrating conditions". Several letters concerning this statement were received. While some agreed with it, others contested its validity.

Dr. Willem Rudolfs, in a 1949 National Lime Association Bulletin, and Gordon J. Wiest⁵, at a Purdue Industrial Waste Conference ten years later, both said, "Under normal hydrating conditions, only the calcium oxide fraction of the dolomitic quicklime will slake". At this point, their opinions diverge. Rudolfs stated that "the magnesium oxide will remain as such". However, he went on to explain that "In recent years, a 'special' or pressure hydrated dolomitic lime had been marketed". Wiest asserts that "The unhydrated magnesium oxide of the dolomitic lime, by reason of its sustained rate of hydration in application, affords a greater available basicity". Brady's⁶ "Materials Handbook" informs us that "When dolomitic quicklime is hydrated, no more than

2 or 3% of the magnesium oxide is converted to the hydroxide, and the lime has a high neutralizing value, useful for neutralization of chemical solutions". Jacobs^{7,8} also reports only a 2 to 3% conversion. Lewis⁹ clarifies the subject by advising that "some dolomitic quicklimes are overburned.....This results in their magnesium oxide component hydrating with difficulty, or not at all, in conventional slakers. The magnesium oxide component of pebble dolomitic quicklime is generally quite active". In the same article, Lewis plotted hydration rates of dolomitic quicklime (Figure 1) at 170°F. The graph appears to indicate that 70% of the MgO in a relatively inactive quicklime will hydrate rapidly. Tadsen,¹⁰ aware of claims to the contrary, offered data at the 1960 Ontario Industrial Waste Conference which indicated to him that "slaking at the higher temperature converts substantially all magnesium oxide to the more soluble magnesium hydroxide". Since all these authorities are quite competent, it would seem logical to conclude that many things are possible.

Hoak, Lewis, Sindlinger, and Hodge¹¹⁻¹⁵ are names familiar to those interested in acid waste neutralization. They have pointed out that it is difficult to calcine dolomite without overburning the magnesia and agree that overburning the lime can make it practically inert. The carbonate of dolomitic lime begins to decompose around 725°C. into calcite and magnesite. The calcite does not begin to decompose until about 900°C. Increasing the temperature above 900°C. is known to increase the volumetric capacity of the kilns. The magnesite decomposes to carbon dioxide and magnesia at about 620°C. Since there is at least a 280°C. difference in optimum calcining temperatures, it would indeed appear to be difficult, if possible, to calcine dolomitic lime without overburning the magnesium oxide or producing a product with above normal amounts of core.

PASTE STORAGE

It would appear safe to admit then that the magnesia hydrates much more slowly than the calcia.

Hoak¹² suggests that "Where magnesian or dolomitic limes are used for neutralization, it is desirable to allow the heavy suspension to age for several days before dilution to a milk suitable for use in neutralization equipment". We do not know of any plant now storing slaked paste, as recommended. Slurry storage has been provided to meet system capacity requirements at peak flows,¹⁶ but hydration times were not studied.

It appears to be common practice to store a dewatered slurry or paste in the mortar industry. Storing the paste improves the plasticity of the putty and also alleviates cracking problems. These quality improvements are generally attributed to the hydration of the magnesia. A special pressure hydrated dolomitic lime is commercially available in which substantially all the magnesium oxide has been converted to magnesium hydroxide. While there appears to be a great demand for the dehydrate within the mortar industry, it has not been used very much for treating waste streams.

The tentative ASTM "Method of Testing Quicklime and Hydrated Lime for Neutralizing Waste Acid" (ASTM Designation C 400-57T) doesn't recommend any substantial storage period for slaked dolomitic lime. It is suggested that one hour be allotted for cooling a paste made with 300 grams of dolomitic quicklime and 275 ml. of 100°F. water prior to running neutralization rate tests.

The idea of storing a paste is not new. It would appear from the curves offered by Lewis⁹ in Figure 1 that storage for only a few hours may be worthwhile. It should be considered at least during the design of the neutralizing systems. This is an area where more research is required. Perhaps storage time requirements could be made part of the ASTM specifications.

SLAKING

The authorities appear to agree, and several state specifically, that both dolomitic and high calcium

quicklime must be slaked prior to reaction with the waste stream. The principal difficulty in slaking is getting effective and rapid contact between the water and all the actual lime particles. The larger the lumps, the more time appears to be needed for penetration of water; the initial wetting of a lump surface seems to result in an encapsulating layer of paste or moist slaked lime which, unless removed, slows the process considerably. This layer can be removed and the slaking accelerated by both heat and physical action. The internal and surface steam formation during slaking accelerates disintegration. Agitation of the mass tends to remove the layer by abrasion.

The capacity of any slaker will depend, to some degree, upon reactivity of the quicklime within the limits of its volumetric capacity. Specific reactivity of the quicklime is a hard parameter to define because it is influenced by so many variables. Perhaps a primary cause of the confusion surrounding this subject is the lack of a simple test which gives a meaningful and complete measure of reactivity. The slaking tests come close. We have used the slaking test described in the American Water Works Association Standard B202-54 entitled "AWWA Standard for Quicklime and Hydrated Lime". Some limes have given only a 10°C. to 12°C. temperature rise after 3 to 5 minutes and we have had some difficulty slaking such quicklime at full capacity.

A tentative revision of the "Standard Methods of Physical Testing of Quicklime and Hydrated Lime" (ASTM Designation C110-58) was issued in 1960. No information was given on what temperature rise could be expected. The Standard does point out that a high reactive lime is generally completely reacted within ten minutes, a medium reactive lime within ten to twenty minutes, and a low reactive lime requires more than twenty minutes to react completely as measured by the time between chemical mixing and the leveling of the temperature-time curve. A proposed revision for the AWWA Standard B202-54 (AWWA Committee 7340-P) follows the same general format. It may, however, suggest that a high reactive lime will show a 40°C. rise in three minutes or less with a water-to-lime

weight ratio of 4:1. A medium reactive lime will show a temperature rise of 40°C. in three to six minutes and a low reactive lime will require more than six minutes to show a temperature rise of 40°C. These proposed revisions give the same suggested reaction times as the tentative ASTM Standards.

There is a subtle indication in some articles that disintegration of the dolomitic lime particles during slaking is indicative of conversion to the hydroxides. We have tested dolomitic quicklime in our paste slaker and the products had a specific surface of 23,000 to 30,000 square centimeters per gram. We feel, however, that the slaking action of the calcia portion could have been the major cause of disintegration.

CHEMICAL ADDITION

To get back on the track, Tadsen,¹⁰ for one, reports that "Dolomitic quicklime...must be slaked (sic) before using for waste neutralization". In the graphs offered by Minnick and Presgrave¹⁷ some neutralization of sulphuric acid must be attributed to the magnesium portion of the dolomite. But, Hoak¹² reports that in one of his tests "a large enough excess of dolomitic lime was added to an acidic waste to raise the pH to 6.5 in about two minutes. In this case, only the lime fraction reacted, and all the magnesium oxide component was found in the sludge". Hoak does interject that he found "the magnesium fraction of lime is most reactive in strongly acid solutions". His subsequent work indicates that neutralization in stages with dolomitic lime would lead to economic chemical usage. In the first tank or stage only enough slaked and stored dolomite is added so that complete reaction brings the pH up to about 4.2. The calcium hydroxide will react first, but when it has reacted there is still some mineral acidity for the magnesium hydroxide to react with (assuming there is a significant amount of magnesium hydroxide there in the first place). The pH may need to be increased for disposal or metals removal. This can be done with high calcium lime or

caustic. Treating the waste in stages can considerably reduce chemical costs.

Hoak, et al¹¹ suggested that economies might be realized by using pulverized high calcium limestone to neutralize the free acid and quicklime, only, to complete the treatment. There will be the problems associated with handling and storing the second chemical and dissipating the carbon dioxide. They also found that the pulverized limestone has "a critical particle size falling between 200 and 325 mesh....for optimum reaction between this material and pickle liquor". They went on to point out that "Dolomitic limestones are practically useless for pickle liquor treatment". We do not know of any proposed standards by which limestones can be judged as a potential neutralizing agent. Boiling in a solution of hydrochloric acid has been suggested and it may mean something but we are afraid that there is only one sure way of assessing the available limestones in your area.

SPECIFIC SURFACE

There are many other areas where there appear to be minor amounts of confusion. Sludge volumes are related to various types of neutralizing agents while in some installations the hydrous metal sludges readily absorb the calcium and/or magnesium precipitates. There are differences in the recommended chemical mixing procedures also. However, there is controversy developing within the industry now that may stimulate a re-evaluation of many presently accepted "facts".

Almost every paper on the subject of lime slaking emphasizes that quicklime should be slaked in hot water to obtain efficient hydration and a suspension of small, reactive, slow settling calcium hydroxide particles. A slightly different viewpoint is expressed in the article entitled "A Study of the Reaction Between Calcium Oxide and Water" by T. C. Miller.¹⁸ Mr. Miller received the 1960 Victor J. Azbe Lime Award for this paper. He expresses the belief that quicklime need not be slaked in warm water. For some applications, he

suggests that slaking in cold water is desirable. Slaking in cold water yields large lime particles, low specific surface, which increase the settling rate of reaction products. Furthermore, he apparently found the specific surface to have little effect on reaction rates. Both viewpoints concur on the relationship between slaking temperature and particle size or specific surface. At the present moment, a dissertation on specific surface, crystal structures, crystal agglomerates, gelatinous insulators, von Weimarn's Law, and the law of mass action fail to resolve the issue.

CONCLUSIONS

The subject of neutralization with lime is not cut and dry. There are some confusing, if not contradictory, statements in the literature. While it may appear to some that the art of designing acid waste treatment facilities has reached the cook book stage, others have found that present standards and design information only emphasize the wisdom of using pilot plants. Standards are now being revised. Old theories are being challenged. Fortunately, many acid waste neutralization plants have been designed and have met treatment standards. Some engineers have found out that acid waste neutralization is not quite as simple as it may seem--in retrospect.

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